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ON THE INHIBITION OF CHEMICAL REACTIONS BY FOREIGN SUBSTANCES. I.

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IN a recent paper[1] attention was called to some very curious phenomena which showed themselves in the oxidation of solutions of stannous chloride by means of free oxygen. These phenomena consist in very marked reduction of the rate of the oxidation as a result of the presence of relatively small quantities of poisonous substances, especially alkaloids. It was, however, seen that potassium cyanide also possessed this power.

It was thought well to delay the further investigation of these curious actions until the course of the reaction between stannous chloride and free oxygen was somewhat more thoroughly understood. The attempt to follow the course of the reaction was successful,[2] but unfortunately, the result was to show that the reaction was complex, taking place in two stages, and on account of this complication, little suited to the investigations in question. It was, therefore, thought advisable to choose another reaction, provided one could be found which would be sensitive to these peculiar agencies.

A solution of arsenic trioxide in water was first tried, but

[1] This Journal, **23**, 140.

[2] *Ibid.*, **23**, 450.

neither in acid, neutral nor alkaline solution was its oxidation rate sufficiently great to allow of its being used without enormous loss of time. Nor was sufficient acceleration produced by previously treating the solution with hydrogen sulphide or after boiling it for some time with arsenic sulphide.[1] The same difficulty was found with ferrous sulphate. Several other substances were tried, but their oxidation rates were found to be either too high (in which case the rate of oxidation is not independent of the action of the apparatus) or too low. Finally a solution of sodium bisulphite was tried and this gave more hopeful indications. The sodium bisulphite used was a commercial product and probably not very pure. Twenty-five cc. of a solution of this substance, of unknown strength, were placed in the shaking apparatus[2] at 25° C. This showed an oxidation rate of 0.2 cc. in three minutes. A trace of copper sulphate raised this to 0.3 cc. in two minutes, and finally the addition of a small quantity of ferrous sulphate raised the rate to 0.5 cc. in one minute. While the absorption was progressing at this last rate, a small quantity of a brucine hydrochloride solution was injected. From this point on the results are given in the following table. In this table $T =$ time in minutes ($T = 0$ = time of injection of brucine).

$V =$ Volume reading on the gas burette.

$\frac{\Delta V}{\Delta T} =$ Average absorption per minute in each interval of observation.

$T =$	0	1	2	3	4	5	6
$V =$	45.5	42.50	40.80	40.00	39.70	39.55	39.45
$\frac{\Delta V}{\Delta T} =$	....	3.00	1.70	0.80	0.30	0.15	0.10
$T =$	7	9	10	15	20	30	38
$V =$	39.40	39.34	39.30	39.05	38.80	38.35	38.00
$\frac{\Delta V}{\Delta T} =$	0.05	0.03	0.04	0.05	0.5	0.045	0.044

At $T =$ thirty-eight minutes, the shaking was discontinued for twenty-two hours. During this time 10.2 cc. had been absorbed. On shaking, the following results were obtained :

$T =$	0	90.
$V =$	27.8	26.60
$\frac{\Delta V}{\Delta T} =$	...	0.013

[1] See Mohr : "Titrir-methode," 1886, p. 364 ; also Young : This Journal, **23**, 143-144.

[2] This Journal, **23**, 119.

Further observations were made with this solution, which need not be recorded here. Gradual reduction of the rate of absorption was noted, due mainly, of course, to the gradual decrease in the concentration of bisulphite.

The results of this first experiment are given here in detail because they afford a good illustration of several of the phenomena to which this paper is devoted. They are: (1) acceleration by means of salts of copper and iron; (2) an initial acceleration upon adding a small quantity of brucine hydrochloride; (3) the rather rapid decrease of the reaction rate thereafter, to a very small value. As the bisulphite showed the phenomena sought in so satisfactory a manner, considerable time has been devoted to its study. It was, however, thought best to use the neutral sulphite as the basis of the solutions studied, as this could be studied equally well in acid, neutral or alkaline solution.

Before passing to a study of the results which are given in the following paper, I wish to suggest a terminology, which must, of course, be considered as subject to change. The phenomena involved are almost wholly new, and something of the sort seems necessary. Bredig,[1] working in a somewhat analogous field, has used the word "poisoning" (Vergiftung) to describe the effect of poisons upon the rate of catalysis by colloidal platinum and gold solutions.

In view of the apparently rather broad analogy existing between physiological poisoning and the phenomena in question one might be almost tempted to follow this usage in the present case. After some thought, it seems to me, however, that such usage is scarcely justifiable at present. In the first place, it is by no means true that the retarding actions under consideration are confined to physiological poisons; and in the second place it is by no means certain that the analogy, in general, is more than superficial. Under these conditions it would seem that the application of the concept of "poisoning" to an entirely new domain is likely to lead to confusion, useless speculation and to superficiality in the investigation of the field. I will, therefore, use the word "inhibition" to cover the phenomena in point, this word having, so far as I am aware, no present technical significance in chemistry. An "inhibitive agent" is then a substance producing an "inhibition," or having an "inhibitive effect." For the

[1] Bredig and Müller von Berneck: *Ztschr. phys. Chem.*, **31**, 258, and later papers.

period beginning with the addition of the inhibitive agent and ending with the time when the inhibitive influence reaches its maximum the true period of development of the inhibition, or more simply, the "development period" will be used. The introduction of these terms, at least for present use, seems to me to be justifiable. The phenomena may naturally be included under the general head of negative catalysis.

It may be stated here that the results following lay no claim to being more than roughly quantitative. No special precautions were taken to purify the distilled water used, and as Bigelow[1] has shown, the character of the distilled water used has a considerable influence upon the rate of oxidation. The object has been solely to study the general character of the phenomena and their scope.

I. THE APPARATUS.

The apparatus used was a modification of the one used in the studies with stannous chloride. The chief modification is of sufficient importance to be sketched here. It lies wholly in the shaking part of the machine. Whereas this in the old machine[2] was fastened in the thermostat tank, in the new one it is wholly independent of this. The great advantage lies in the avoidance of the jarring and shaking of the thermostat, which sometimes, in the old machine, threatened to fall from its supports, and required constant vigilance. The new apparatus will run indefinitely without attention. The new arrangement is shown in Fig. 1. It consists of a stout wooden stand which can be raised and lowered at will. In the two horizontal arms of this stand are fixed four stout rods of $^1/_4$ inch brass, *a*, *a*, *a*, *a*, which are

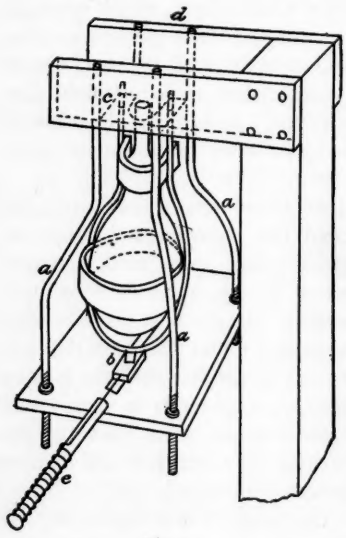


Fig. 1.

[1] *Ztschr. phys. Chem.*, **26**, 493.

[2] This Journal, **23**, 121.

doubly curved as in the drawing. The lower ends of these rods are threaded for a distance of about 4 inches. Upon these rods is supported a rectangular brass plate, $^1/_8$ inch thick, with $^1/_4$ inch holes at each corner. This platform is fastened to the rods by means of two nuts on each rod, one above and one below the plate. These, when screwed tight, hold the platform very firmly in place, and furthermore allow of adjusting the height of the platform, as may be desired.

Down the middle of the platform longitudinally is cut a slot in which runs a small carriage, *b*, also of brass. This slides freely back and forth in the slot, and is provided with a simple device for attaching the bottom of the carrier in which is held the flask. This carrier is the same as was used in the experiments with stannous chloride. The brass rods at the top of this carrier pass through holes in the brass plate *c* which is fastened to one of the horizontal arms of the wooden stand. The whole carrier and flask are thus easily removable from the apparatus. The shaking is brought about by an electric motor with variable resistance to regulate speed. A stout gut cord passes from the crank of the motor over a pulley fastened on the back of the far arm of the wooden stand (near *d*), thence downward under a second pulley (not shown) fastened at the far end of the brass platform. Thence it runs to the carriage *b*, to which it is fastened. The return of the flask to its original position after being pulled to the far end of the platform, is brought about by the spiral spring *e* of hardened brass wire. As a matter of fact, two such springs are used, one fastened to the carrier above, and the other below the platform. This insures more even working of the carriage in the slot. Simple devices allow of the regulation of the length of stroke, and of the tension of the springs. Having once gotten the apparatus in order, I have used it for nearly four months, almost daily, and some times for eight hours per day, without the necessity for the slightest repair or alteration, except that one gut string had to be replaced.

The method used in the following experiments was the same as was used in the studies with stannous chloride, and for further details the reader must be referred to that paper.

2. SCOPE OF THE PHENOMENON OF INHIBITION.

So far as I am aware almost all reactions which have hereto-

fore shown the phenomenon of inhibition, *i. e.*, a marked reduction of the reaction rate under the influence of minute quantities of foreign substances, are reactions in which free oxygen is concerned in some way or other. Exceptions are apparently to be found in some cases, in the action of enzymes.

The reactions which are of the greatest importance for us here may be divided into two groups: (1) reactions in which hydrogen peroxide is decomposed with the evolution of free oxygen; (2) the voluntary (and catalytically accelerated) oxidation of certain substances by free oxygen. The literature bearing upon the first group has been brought together and materially extended by Bredig and his coworkers.[1]

In this group we have to do always with a deadening of the efficiency of a positive catalysor or accelerator. Among these catalysors we find certain organic ferments, platinum foil and black and colloidal platinum and gold solutions. The accelerating action of these substances is greatly diminished by the addition of minute quantities of a great variety of substances, including hydrogen sulphide, carbon bisulphide, hydrocyanic acid, mercuric chloride, etc. The catalytic action of the blood corpuscles is also reduced by minute traces of hydrocyanic acid. Bredig[2] states that strychnine is apparently without action in the catalysis of hydrogen peroxide by means of colloidal platinum.

In the second group we have to do with reactions in some cases, which are apparently not catalytically accelerated in the first place, *i. e.*, with a true negative catalytic effect.[3] All such cases, so far as I know, are reactions of oxidation by means of free oxygen. Among these are to be mentioned: (1) the influence of small quantities of foreign substances in oxygen upon the glowing of phosphorus;[4] (2) the phenomena observed by Bigelow[5] in connection with the oxidation of sodium sulphite by the oxygen of the air; (3) the phenomena involved in the oxidation of stannous chloride by means of oxygen.[6] A case of reduction of

[1] Bredig and Müller von Berneck: *Loc. cit*; Bredig and Ikeda: *Ztschr. phys. Chem.*, **37**, 1; Bredig and Reinders: *Ibid.*, **37**, 323.

[2] *Loc. cit.*

[3] We may, for convenience, distinguish between "apparent" negative catalysis, or the reduction of the activity of a positive catalysor, and "true" negative catalysis, or the reduction of the rate of a reaction occurring without previous catalytic acceleration.

[4] The literature of this subject together with new results is to be found in a paper by Centnerzwer: *Ztschr. phys. Chem.*, **26**, 1.

[5] Bigelow: *Ibid.*, **26**, 493.

[6] *Loc. cit.*

reaction rate in an already catalytically accelerated oxidation was found by Ernst[1] in the oxidation of hydrogen by oxygen in presence of a colloidal platinum solution. The same phenomenon with platinum foil was observed by Faraday.

In order to gain some idea of the scope of these inhibitive actions in the oxidation of sodium sulphite, several experiments were carried out by me upon the oxidation by means of agents other than oxygen. The substances chosen were nitrous and nitric oxides; both being gases, the phenomena allowed of being studied in the apparatus with which I was working.

a. Experiments with Nitrous Oxide.—The experiments with nitrous oxide were carried out exactly according to the method described in the previous paper[2] for studying the oxidation of stannous chloride. The nitrous oxide was prepared from ammonium nitrate and stored for use in a gas-holder. On beginning the experiment, a very marked decrease in the volume of the gas in the burette was noticed, due, of course, to the solubility of nitrous oxide in the solution. After this first rapid absorption had ceased, measurements were begun. After a time a quantity of brucine hydrochloride solution was added and measurements continued. The results of two series of measurements are given below. In the first series water was used in the gas burette. As it was thought that the slow decrease in volume might possibly be due to gradual absorption of the gas by the water in the burette, mercury was used in the second experiment, and this was, futhermore, allowed to stand for a couple of days after the measurements were discontinued in order to see to a certainty whether a reaction really occurred. T is given in minutes.

EXPERIMENT 1.

					1 cc. $\frac{m}{10}$ brucine hydrochloride added.[3]		
$T =$	0	10	20	30	0	10	20
$V =$	36.2	35.85	35.5	35.2	35.45	35.10	34.75
$\frac{\Delta V}{\Delta T} =$	....	0.035	0.035	0.035	....	0.035	0.035

After making the solution slightly acid the rate of absorption remained unchanged.

[1] Ernst: *Ztschr. phys. Chem.*, **37**, 448.

[2] *Loc. cit.*

[3] m is used here to represent the molecular or "molar" weight. *Cf.* Noyes: This Journal, **23**, 41.

EXPERIMENT 2.

	Mercury in gas burette.				1 cc. $\frac{m}{10}$ brucine hydrochloride added.		
$T =$	0	5	10	15	0	5	10
$V =$	39.7	39.55	39.40	39.20	39.35	39.15	38.95
$\frac{\Delta V}{\Delta T} =$	...	0.03	0.03	0.04	...	0.04	0.04

The volume after standing for twenty-four hours had decreased to 28.2 cc. After forty-eight hours to 19.3 cc. Thus during the whole time over 20 cc. of the gas had been absorbed, which shows conclusively that a reaction of some sort takes place. The evidence of both sets of observations goes to show, however, that the rate of this reaction is not measurably influenced by the addition of the indicated amount of brucine hydrochloride solution. The sulphite solution used in these experiments contained 2.5 grams of crystallized sulphite per 100 cc. of solution. As will be shown later the amount of brucine used here would have sufficed in case of oxidation with oxygen to have reduced the rate to $^1/_{15}$, or less, of its original value. The conclusion would seem to be justified that the reaction between nitrous oxide and sodium sulphite is uninfluenced by brucine.

b. Experiments with Nitric Oxide.—The first few attempts to follow the reaction between sodium sulphite and nitric oxide showed that the reaction goes too rapidly to be measured with certainty in the apparatus in use, and the same was found true of stannous chloride. A 0.2 normal solution of stannous chloride absorbed the gas at the rate of about 25 cc. per minute. No measurable influence was exerted by the addition of relatively large quantities of brucine hydrochloride. A solution of 5 grams of sodium sulphite in 200 cc. of solution gave approximately the same result. With such rapid absorption it is probable that it is more nearly the absorption rate than the oxidation rate that is measured. By using a solution only one-half as strong as the above, the rate was still too rapid for certainty. The results of such a series is given here. As will be seen the addition of the brucine hydrochloride has again no noticeable effect. Time in minutes:

			Added 1 cc. $\frac{m}{10}$ brucine hydrochloride.							
$T =$	0	½	1	1½	2½	3½	4½	6½	7½	10
$V =$	47.0	40.7	36.7	33.2	26.4	17.7	9.9	20.6	20.5	20.4
$\Delta V =$	...	6.3	4.0	3.5	6.8	8.7	7.8	−10.7	+0.1	+0.1

An inspection of these results shows no appreciable drop in the reaction rate upon addition of the brucine hydrochloride, or at least none in any way comparable with the drop noticed (see later) in results with oxygen. A most marked feature of the results is seen in the fact that the gas volume at first rapidly decreases, then increases very rapidly and finally very slowly decreases again. Several experiments showed this to be a constant phenomenon and use was made of it to determine, if possible, an influence of the alkaloid upon the rate or course of the reaction. Several series of observations were made upon solutions without addition of brucine hydrochloride and several with addition of this reagent. T in minutes:

a. Results without Brucine.

1.			2.			3.			4.		
T.	V.	ΔV.	T.	V.	ΔV.	T.	V.	ΔV.	T.	V.	ΔV.
0	49.0	....	0	50.0	....	0	46.5	....	0	50.0	....
½	39.0	+10.0	½	45.0	+5.0	½	37.5	+ 9.0	½	39.0	+11.0
1	32.5	+ 6.5	1	42.0	+3.0	1	32.5	+ 5.0	1	30.5	+ 8.5
1½	26.0	+ 6.5	1½	38.5	+3.5	1½	27.0	+ 5.5	1½	22.5	+ 8.0
2	20.5	+ 6.5	2	35.5	+3.0	2	22.0	+ 5.0	2	16.5	+ 6.0
2½	15.5	+ 5.0	2½	30.0	+5.5	2½	18.0	+ 4.0	2½	14.2	+ 2.3
3	11.2	+ 4.3	3	25.4	+4.6	3	14.0	+ 4.0	3	21.5	— 7.3
3½	8.0	+ 3.2	3½	22.4	+3.0	3½	10.8	+ 3.2	3½	22.4	— 0.9
3⅚	6.5	+ 1.5	4	20.5	+1.9	4	8.5	+ 2.3	4	22.3	+ 0.1
4¼	11.0	— 4.5	4½	17.3	+3.2	4½	10.0	— 1.5	5	22.2	+ 0.1
4½	19.0	— 8.0	5	15.2	+2.1	5	20.0	—10.0			
5	21.4	— 2.4	5½	17.5	—1.8	5½	21.0	— 1.0			
6	21.1	+ 0.3	6	25.5	—8.5	8	20.6	+ 0.4			
8	20.9	+ 0.2	6½	25.8	—0.3	10	20.5	+ 0.1			
			7	25.65	+0.15	35	19.8	+ 0.7			
			8	25.4	+0.25	42 hrs.	5.1	+14.7			

b. Results with Brucine Hydrochloride.—In these experiments, the brucine hydrochloride was added before beginning the experiment. One cc. of $\frac{m}{10}$ brucine hydrochloride was used.

1.			2.			3.		
T.	V.	ΔV.	T.	V.	ΔV.	T.	V.	ΔV.
0	50.0	....	0	50.0	...	0	50.1	....
½	43.0	+ 7.0	½	38.0	+ 12.0	½	38.0	+ 12.0
1	37.0	+ 6.0	1	31.0	+ 7.0	1	26.0	+ 12.0
1½	31.0	+ 6.0	1½	26.0	+ 5.0	1½	19.0	+ 7.0
2	25.7	+ 5.3	2	24.5	+ 1.5	2	24.0	— 5.0
2½	21.5	+ 4.2	2½	23.5	+ 1.0	2½	29.5	— 5.5
3	19.0	+ 2.5	3	23.1	+ 0.4	3	29.6	— 0.1
3½	28.0	— 9.0	3½	26.0	— 2.9	5	29.4	+ 0.2
4	28.3	— 0.3	4	30.9	— 4.9			
5	28.2	+ 0.1	5	30.6	+ 0.3			

In the experiments without brucine hydrochloride, the turning-point in the volume reading occurred after respectively $3^5/_6$, 5, 4, and $2^1/_3$ minutes. With brucine, after respectively 3, 3, and $1^1/_2$ minutes. Without brucine hydrochloride, the turning-point occurred after the following volumes had been absorbed: 42.5 cc., 34.8 cc., 38 cc., and 35.8 cc.; with brucine hydrochloride, after respectively 31 cc., 27 cc., and 31 cc. had been absorbed.

The variations in all these results are undoubtedly due mainly to variations in the rate of shaking and in variations in local conditions, such as slight differences in the form of the flasks used, which might make much difference in the surface of the liquid exposed and consequently, at these high rates, in the oxidation rate. On the whole there are no more marked variations between the two series than between different experiments of either series, and the conclusion seems to be justifiable that the brucine hydrochloride exerts no influence upon the rate of the reaction, or if it does that its influence is of a wholly different order of magnitude from the influence exerted upon the oxidation by means of free oxygen.

Thus the evidence at hand seems to point rather distinctly toward the probability that the inhibitory actions in question are quite closely confined to reactions in which free oxygen is involved. Of course this point cannot be considered as definitely settled until a vastly greater amount of evidence is accumulated.[1]

3. PRELIMINARY EXPERIMENTS TO DETERMINE WHAT CLASSES OF SUBSTANCES SHOW INHIBITIVE ACTION.

A large number of experiments were carried out to determine how wide-spread the phenomenon of inhibition of the reaction between oxygen and sodium sulphite solution might be. The method of experimentation was to place 25 cc. of the sulphite

[1] The anomalous conduct of the reaction with nitric oxide and sodium sulphite is readily explained upon the assumption that the nitric oxide at first reacts with the sulphite, forming an unstable compound which then rather rapidly breaks down with the evolution of some other gas. The final slow decrease in volume may be due merely to a residue of the original reaction between the much diluted reagents, or it may be due to the fact that the gas evolved is some substance capable of further reaction. In looking up the literature on this matter we find that nitric oxide, when conducted into an alkaline solution of sodium sulphite, yields nitrosohydroxylamine sulphonic acid in form of the sodium salt $Na_2SN_2O_5$. (Raschig: *Ann. Chem.* (Liebig), **241**, 230.) These salts show a tendency to decompose into sulphates and nitrous oxide. Several experiments made in my laboratory by Mr. Bruno Olshausen show that the ratio between the volume of nitric oxide absorbed and the volume of the gas given off is very nearly 2:1. The phenomena referred to above are thus readily explained, since, as has been previously shown, nitrous oxide itself seems to be slowly absorbed by sodium sulphite solutions.

solution in the flask of the shaking apparatus, to determine the rate of oxidation before any foreign substance was added, then to add an amount of the substance to be tested sufficient to make the solution approximately $^1/_{200}$ molar. Usually 1 cc. of a $^1/_{10}$ molar solution was used for this purpose. The solutions of sodium sulphite used from his point on were always prepared by dissolving 2.5 grams of the crystallized salt in 200 cc. of distilled water. These solutions were approximately $^8/_{100}$ normal. For this particular investigation, a knowledge of the exact strength of the solutions was wholly unnecessary. It was considered wise to prepare a fresh solution about every two hours, mainly because of the rather marked change in the oxidation rate of the solution on standing. The flasks used were cleaned after each experiment by soaking in chromosulphuric acid mixture. This was found necessary, as after simple washing with water, no matter how carefully done, there seemed to remain always enough of the foreign substance to throw out the results of the following set of observations. In working in neutral and alkaline solutions air was used instead of pure oxygen on account of the too rapid rate of oxidation with the latter.

a. Experiments with Brucine Hydrochloride.

The first substance investigated was brucine hydrochloride. This was found to possess a most marked inhibitive action in neutral solution, as the following measurements show (time in minutes):

1

	Before adding brucine hydrochloride.			After adding brucine hydrochloride.			
$T =$	0	1	2	0	1	2	3
$V =$	49.25	47.90	46.60	46.20	46.05	45.95	45.85
$\frac{\Delta V}{\Delta T} =$	...	1.35	1.30	...	0.15	0.10	0.10

2

$T =$	0	1	0	1	2	3
$V =$	50.00	48.50	48.50	48.40	48.3	48.22
$\frac{\Delta V}{\Delta T} =$	...	1.50	...	0.10	0.10	0.08

In slightly alkaline solution, the inhibitive action of brucine hydrochloride is vastly greater than in neutral solution. This is shown by the following experiment in which such a weakly alkaline solution was used, the concentration of brucine hydrochloride being the same as above; *viz.*, $^1/_{200}$ molar.

	Before adding brucine hydrochloride.			After adding brucine hydrochloride.			
$T =$	0	1	2	0	1	2	17 hours.
$V =$	50.00	48.60	47.45	46.90	46.90	46.90	46.90
$\frac{\Delta V}{\Delta T} =$	....	1.40	1.15	....	0.00	0.00	0.00

That is, aften seventeen hours, no measurable oxidation had taken place.

This enormous increase of inhibitive action in alkaline over neutral solution is, perhaps, even more strikingly shown in the following set of observations. In this case, the original solution was neutral and, after determining the normal rate, 1 cc. of a 0.0001 molar solution of brucine hydrochloride was added. This made the solution finally $^1/_{260{,}000}$ molar in brucine. The result, as will be seen, was an extremely small, if any, reduction of the oxidation rate. Next, a few drops of dilute potassium hydroxide solution were added. The enormous drop in the rate upon this may be seen from the figures:

Before adding brucine hydrochloride.			After adding brucine hydrochloride.			After adding potassium hydroxide.		
T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	50.00	...	0	44.90	...	0	41.40	....
1	47.50	2.50	1	43.00	1.90	1	41.20	0.20
2	45.30	2.20	2	41.60	1.40	50	40.94	0.005
						40 hours	39.75	0.016

As will be seen the rate is reduced to something less than 0.01 of the normal rate by the presence in alkaline solution of a quantity of brucine hydrochloride of the concentration of $^1/_{200{,}000}$ molar.

In acid solution the influence of brucine hydrochloride is much less than in neutral solution and the period of development of the inhibition is much longer. The oxidation in weakly acid solution takes place very slowly and in most of the experiments under these conditions, the reaction was accelerated by means of a few drops of a solution of mixed copper and iron sulphates. The whole phenomenon in acid solution is quite complex and could be given here only with the aid of many words. The discussion of this point will be left therefore until later.

b. Experiments with Quinine Bisulphate.

Quinine was the next alkaloid studied and it was used in the form of the bisulphate. Some objection attaches to the use of an acid salt for this purpose, since the presence of free hydrogen

ions markedly influences the reaction rate, and since further the influence of quinine in acid solution is also much less than in neutral or alkaline solution. Still the influence even with the acid salt is so clear and sharply defined as to leave the matter in no sort of doubt. I give here only a limited number of measurements to illustrate the action of quinine bisulphate. Many more were made, but there is no particular need of giving them here, as the same phenomenon was always observed under the same conditions.

The following figures show the influence of quinine bisulphate in neutral solution. The quantity of the alkaloid added was 1 cc. of a 0.1 molar solution, thus making the whole solution $^1/_{200}$ molar.

Before.			After.					
T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	45.00	...	0	44.10	...	6	41.10	0.52
1	44.18	0.82	1	43.70	0.40	7	40.64	0.46
			2	43.22	0.48	8	40.18	0.46
			3	42.70	0.52	9	39.75	0.43
			4	42.16	0.54	10	39.30	0.45
			5	41.62	0.54			

As will be seen there is at first a very marked reduction, to a little less than one-half. The rate, however, increases noticeably for about five minutes. The cause of this was easily found. After the experiment was discontinued, the solution in the flask was found to contain a considerable quantity of a glittering white crystalline substance. This is probably a very slightly soluble compound of quinine with sodium sulphite. Brucine shows the same phenomenon but to a very much smaller degree. The explanation of the increasing absorption rate is, however, readily explained since there is formed first a solution supersaturated as to the quinine compound. This then gradually crystallizes out, thereby reducing the concentration of the quinine and to some extent nullifying the inhibitive action. On account of this peculiar conduct an experiment with a solution of quinine bisulphate only one-tenth as strong as above is reported here. This is nearly but not quite free from the increasing reaction rate, but still shows a marked inhibitive influence on the part of the quinine, even though its concentration in the solution was only $^1/_{2600}$ molar.

Before.			After.					
$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.	$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.	$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
0	45.00	...	0	44.00	...	8	40.58	0.42
1	44.19	0.81	1	43.62	0.38	9	40.20	0.38
			2	43.20	0.42	10	39.84	0.36
			3	42.75	0.45	11	39.53	0.31
			4	42.30	0.45	12	39.28	0.25
			5	41.84	0.46	13	39.05	0.23
			6	41.42	0.42	14	38.87	0.18
			7	41.00	0.42			

As is to be seen the inhibitive action of quinine in neutral solution appears to be considerably less than that of brucine. This is possibly due to the influence of the free acid of the acid sulphate since in alkaline solution the quinine seems nearly as powerful as brucine. Following are the results of an experiment in weakly alkaline solution. The solution was made $^1/_{2600}$ molar in quinine.

Before.			After.		
$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.	$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
0	45.00	...	0	43.50	...
1	43.65	1.35	1	43.40	0.10
			2	43.40	0.00
			5	43.40	0.00

That is, in alkaline solution, $^1/_{2600}$ molar quinine is sufficient to practically stop the oxidation of the sodium sulphite. This solution was $^1/_{10}$ normal in potassium hydroxide.

In acid solution quinine conducts itself very much as does brucine.

c. Experiments with Morphine Hydrochloride.

In this and all following experiments of this group of preliminary investigations, the method of procedure was the same as was used with brucine hydrochloride and with quinine bisulphate. In some cases, where the result in neutral solution was very decisive, the test in alkaline solution was omitted:

$^1/_{260}$ *Molar Morphine Hydrochloride.*

A.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
Before.		
0	45.00	....
1	43.30	1.70
After.		
0	43.30	....
1	42.96	0.34
2	42.80	0.16
3	42.65	0.15
4	42.50	0.15
5	42.35	0.15
10	41.68	0.134
15	41.23	0.092
45	38.90	0.077

B.

	Before.	
0	45.00	....
1	43.98	1.02
	After.	
0	44.00	....
1	43.94	0.06
2	43.88	0.06
3	43.82	0.06
4	43.76	0.06
5	43.70	0.06
10	43.42	0.056
15	43.10	0.060

d. $^1/_{260}$ *Molar Atropine Sulphate.*

T.	*V.*	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	42.90	2.10
	After.	
0	42.70	....
1	42.25	0.45
2	41.83	0.42
3	41.45	0.38
4	41.10	0.35
5	40.75	0.35
10	39.33	0.284
15	38.30	0.206
20 hrs.	34.40	....
60 hrs.	31.00	....

e. $^1/_{260}$ *Molar Cane-Sugar.*

T.	*V.*	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.35	1.65
	After.	
0	43.20	....
1	42.76	0.44
2	42.46	0.30
3	42.20	0.26
4	41.90	0.30
5	41.63	0.27
6	41.38	0.25
7	41.12	0.26
8	40.88	0.24
9	40.66	0.22
10	40.43	0.23

Added here 1 cc. normal potassium hydroxide.

0	40.20	....
5	40.20	0.00
10	40.20	0.00
15	40.20	0.00

f. $^1/_{260}$ *Molar Glycerine.*

T.	*V.*	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.10	1.90
	After.	
0	42.70	....
1	42.30	0.40
2	42.08	0.22
3	41.86	0.22
4	41.08	0.18
5	41.50	0.18
10	40.60	0.18

Added here 1 cc. normal potassium hydroxide.

0	40.48	....
1	40.30	0.18
6	40.30	0.00
11	40.30	0.00
16	40.30	0.00

g. $^1/_{260}$ *Molar Potassium Cyanide.*

T.	*V.*	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.10	1.90
	After.	
0	43.00	....
1	42.00	1.00
2	41.53	0.47
3	41.30	0.23
4	41.10	0.20
5	40.90	0.20
6	40.75	0.15
7	40.63	0.12
8	40.50	0.13
9	40.38	0.12
10	40.26	0.12

Added here 1 cc. normal potassium hydroxide.

0	40.20	....
1	39.95	0.250
6	39.92	0.006
11	39.82	0.020
16	39.80	0.004
21	39.80	0.000
26	39.80	0.000
31	39.80	0.000

h. $^1/_{260}$ *Molar Ammonium Chloride.*

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	42.55	2.45
	After.	
0	42.50	....
1	41.25	1.25
2	39.95	1.30

Added here 1 cc. normal potassium hydroxide.

0	39.70	....
1	39.30	0.40
10	39.20	0.022
20	39.10	0.010
30	39.10	0.000
50	39.10	0.000
24 hrs.	39.10	0.000

i. $^1/_{260}$ *Molar Sodium Acetate.*

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	42.90	2.10
	After.	
0	42.70	....
1	41.10	1.60

Added here 1 cc. normal potassium hydroxide.

0	40.80	....
1	39.25	1.55
2	38.60	0.65
3	38.25	0.35
4	38.00	0.25
5	37.80	0.20
10	37.16	0.13
15	36.78	0.08
20	36.56	0.044

j. $^1/_{260}$ *Molar Pyrogallol.*

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	42.20	2.80
	After.	
0	42.00	....
1	41.85	0.15
2	41.83	0.02
3	41.81	0.02
4	41.80	0.01
5	41.78	0.02
10	41.73	0.01
15	41.63	0.02
20	41.56	0.014
25	41.50	0.012

Added here 1 cc. normal potassium hydroxide.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
0	41.50	....
1	39.00	2.50
2	37.20	1.80
3	36.30	0.90
4	36.10	0.20
5	35.93	0.17
10	35.84	0.018
20	35.78	0.006
30	35.76	0.002
40	35.71	0.005
54	35.67	0.004
18 hrs.	33.50	....

In these results for pyrogallol attention is to be called to the very great, but rapidly decreasing, acceleration upon addition of the potassium hydroxide solution. It is, of course, due to the absorption of oxygen by the pyrogallol itself, which takes place

slowly in neutral, but rapidly in alkaline, solution. This phenomenon, however, gives a possible clue to the explanation of all initial accelerations of this sort, and will be treated more in detail in a later paper.

k. Experiment with $^1/_{260}$ Molar Resorcinol.

T.	V.	$\frac{\Delta V}{\Delta T}$
	Before.	
0	45.00	...
1	42.70	2.30
	After.	
0	42.40	...
1	42.10	0.30
2	41.87	0.23
3	41.68	0.19
4	41.48	0.20
5	41.28	0.20
Added here 1 cc. normal potassium hydroxide.		
0	41.10	...
1	40.80	0.30
6	40.80	0.00
11	40.80	0.00
42 hrs.	40.50	...

l. $^1/_{260}$ Molar p-Oxybenzoic Acid.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.05	1.95
	After.	
0	43.00	...
1	41.70	1.30
Added here 1 cc. normal potassium hydroxide.		
0	41.60	...
1	40.40	1.20
2	40.33	0.07
3	40.28	0.05
4	40.28	0.00
5	40.28	0.00
2½ hrs.	40.28	0.00

m. $^1/_{260}$ Molar Hydroxylamine Hydrochloride.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.70	1.30
	After.	
0	43.68	...
5	43.68	0.00
25	43.68	0.00
35	43.68	0.00

n. $^1/_{260}$ Molar Ethyl Alcohol.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	42.80	2.20
	After.	
0	42.80	...
1	42.58	0.22
2	42.44	0.14
3	42.30	0.14
4	42.17	0.13
5	42.05	0.12
Added here 1 cc. normal potassium hydroxide.		
0	42.00	...
1	41.60	0.40
6	41.60	0.00
11	41.60	0.00
24 hrs.	41.55	...

As the preceding studies show, the power to inhibit the oxidation rate of sodium sulphite to a very marked degree belongs to the most diverse organic compounds, as well as to ammonium compounds, hydroxylamine, and potassium cyanide, and in all cases, this power is vastly greater in alkaline than in neutral solution. Further, this inhibitive action is of noticeably different intensity in different cases, although in most cases in alkaline solution, the effect is so great in $^1/_{260}$ molar solution as to practically totally stop the reaction. In addition to the substances here studied, Bigelow[1] has shown that the power belongs, also, to mannite, succinic and tartaric acids, benzaldehyde, phenol, the three cresols, acetone, several alcohols and aniline. It would thus seem safe to say that this inhibitive action is characteristic to greater or less degree of all organic matter, and in addition, of many nitrogen compounds not organic. That the power belongs distinctly to ordinary distilled water, which contains traces of organic matter and of ammoniacal, or at least proteid, substances is shown very clearly by all attempts that I have made to obtain concordant results with simple water solutions. In such cases, the reaction rate always falls off very markedly toward the end of the reaction. Bigelow also noticed the same phenomenon.

4. EXPERIMENTS TO DETERMINE THE MINIMUM CONCENTRATION OF SEVERAL SUBSTANCES WHICH IS NECESSARY TO PRODUCE MEASURABLE INHIBITION.

In order to determine the minimum concentration of different substances which are capable of producing measurable inhibition a few substances were chosen and each subjected to the following treatment:

(1) A 0.1 molar solution of each substance was prepared and, from this, by successive dilution, were prepared solutions which were respectively 0.01, 0.001, 0.0001, etc., etc., molar.

(2) In each experiment, the normal rate of oxidation of 25 cc. of a solution of 2.5 grams of crystallized sodium sulphite in 200 cc. of distilled water was determined. One cc. of the reagent to be investigated was then added and the rate again measured, the observations being, in general, continued for a considerable time. The concentration of the reagent in the solution is, under these

[1] *Loc. cit.*

conditions, $^1/_{26}$ of that of the reagent added; *i.e.*, by using a 0.001 molar reagent, the solution becomes $^1/_{26,000}$ molar.

(3) Observations were begun in $^1/_{260}$ molar solution and continued with increasing dilution until the reagent failed to produce a noticeable effect.

(4) Each reagent was tested in alkaline and neutral, and sometimes in acid solution. In acid solution, oxygen was used, and in alkaline and neutral solutions, air was used.

The substances investigated in this manner were: Brucine hydrochloride, quinine bisulphate, morphine hydrochloride, cane-sugar and ammonium chloride.

A. Experiments with Brucine Hydrochloride.

1. In Neutral Solution.—The following tables show the results of several series of measurements with brucine hydrochloride:

TABLE I.—$^1/_{260}$ MOLAR BRUCINE HYDROCHLORIDE.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	50.00	...	0	48.50	...
1	48.50	1.50	1	48.40	0.10
			2	48.30	0.10
			3	48.22	0.08

TABLE II.—$^1/_{2600}$ MOLAR BRUCINE HYDROCHLORIDE.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	50.00	...	0	48.45	...
1	48.50	1.50	1	47.90	0.55
			2	47.35	0.55
			3	46.90	0.45
			4	46.50	0.40
			5	46.10	0.40
			6	45.70	0.40

TABLE III.—$^1/_{26,000}$ BRUCINE HYDROCHLORIDE.

Before.			After.		
T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	50.00	...	0	48.20	...
1	48.50	1.50	1	46.90	1.30
			2	45.70	1.20
			3	44.70	1.00
			4	43.80	0.90

TABLE IV.—$^1/_{260,000}$ BRUCINE HYDROCHLORIDE.

A.

Before.			After.		
$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.	$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
0	50.00	...	0	48.30	...
1	48.35	1.65	1	46.65	1.65
			2	45.10	1.55
			3	43.50	1.60
			4	42.00	1.50

B.

0	50.00	...	0	44.90	...
1	47.50	2.50	1	43.00	1.90
2	45.30	2.20	2	41.60	1.40

As is to be seen from the above tables, the inhibitive action of brucine hydrochloride becomes too small to be detected in neutral solution at a concentration of $^1/_{260,000}$ molar. Even at $^1/_{260,000}$ molar, the initial effect is extremely small if at all present, the values of $\frac{\Delta V}{\Delta T}$ being so little smaller after than before the addition of the brucine hydrochloride that they are not readily distinguishable from normal values which would naturally decrease, owing to decreasing concentration both of sulphite and oxygen.

It is fairly safe to place the limit of the concentration at which the brucine hydrochloride shows measurable inhibitive effect at somewhere near $^1/_{26,000}$ molar, although, as later results will show, it is probably considerably less than this. In these earlier measurements, the significance of the "development period" was not fully realized.

2. *In Alkaline Solution.*—Preliminary experiments showed that brucine hydrochloride in alkaline solution exerts a vastly greater inhibitive action than in neutral solution. Therefore it is not necessary to give space here to tables of results obtained by using less than $^1/_{26,000}$ molar brucine hydrochloride. As will be seen, the inhibition even at this dilution is practically complete.

TABLE V.—$^1/_{26,000}$ BRUCINE HYDROCHLORIDE.

A.

$^1/_{40}$ Potassium Hydroxide.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	49.00	...
1	48.58	0.42
2	48.18	0.40
3	47.78	0.40
	After.	
0	47.70	...
1	47.54	0.16
2	47.50	0.04
3	47.47	0.03
4	47.45	0.02
5	47.44	0.01
10	47.40	0.008
15	47.40	0.000

B.

$^1/_{10}$ Potassium Hydroxide.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.80	1.20
	After.	
0	43.70	...
1	43.60	0.10
2	43.58	0.02
3	43.58	0.00
4	43.58	0.00
5	43.58	0.00

TABLE VI.—$^1/_{260\cdot000}$ BRUCINE HYDROCHLORIDE.

A.

$^1/_{40}$ Potassium Hydroxide.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	49.00	...
1	48.20	0.80
2	47.55	0.65
3	46.90	0.65
	After.	
0	46.80	...
1	46.34	0.46
2	46.05	0.29
3	45.78	0.27
4	45.54	0.24
5	45.32	0.22
6	45.10	0.22
7	44.90	0.20
8	44.70	0.20
9	44.50	0.20
10	44.30	0.20

B.

$^1/_{10}$ Potassium Hydroxide.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.47	0.53
2	43.93	0.54
3	43.48	0.45
	After.	
0	43.40	...
1	42.90	0.50
2	42.50	0.40
3	42.23	0.27
4	42.08	0.15
5	42.00	0.08
6	41.93	0.07
7	41.87	0.06
8	41.83	0.04
9	41.80	0.03
10	41.77	0.03
11	41.75	0.02
12	41.73	0.02
13	41.72	0.01
14	41.71	0.01

TABLE VII.—$^1/_{2'600\cdot000}$ BRUCINE HYDROCHLORIDE.

A.

$^1/_{40}$ Potassium Hydroxide.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	44.00	...
1	43.49	0.51
2	43.00	0.49
3	42.50	0.50
	After.	
0	42.30	...
1	41.73	0.57
2	41.30	0.43
3	40.90	0.40
4	40.52	0.38
5	40.17	0.35

B.

$^1/_{10}$ Potassium Hydroxide.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.48	0.52
2	43.92	0.56
3	43.40	0.52
	After.	
0	43.30	...
1	42.66	0.64
2	42.05	0.61
3	41.50	0.55
4	41.00	0.50
5	40.53	0.47
10	38.92	0.322
15	38.13	0.158
20	37.58	0.110
21	37.50	0.08

An inspection of the above tables shows that in $^1/_{26,000}$ molar solution brucine acts so powerfully as to inhibit practically totally the oxidation of sodium sulphite in alkaline solution. The inhibition is complete in a somewhat shorter time in $^1/_{10}$ normal alkaline solution than in $^1/_{40}$ normal. In $^1/_{26,000}$ molar concentration the inhibition is still very marked, especially in $^1/_{10}$ normal alkaline solution. Here, after a little over 3 cc. of oxygen have been absorbed, the rate has fallen from about 0.5 cc. per minute to 0.01 cc. per minute. In $^1/_{40}$ normal alkaline solution the rate has fallen, after about the same amount of oxygen has been absorbed, to about one-third the original rate. The 25 cc. of the solution used would require for complete oxidation about 13–14 cc. of oxygen (calculated from titration numbers). Thus, neglecting change in concentration of oxygen, as this is relatively insignificant, the fall in the volume absorbed per unit of time under the above conditions should be less than one-fourth. We find with $^1/_{40}$ normal alkali a drop of about two-thirds which distinctly indicates inhibitive action. As to the presence of inhibitive action in 0.1 normal alkaline solution there can be no doubt, as it is very nearly complete.

In $^1/_{2,600,000}$ molar brucine hydrochloride and 0.1 normal potassium hydroxide the rate has fallen, after about one-half has been oxidized, to about one-seventh of the initial rate. Without inhibition it should have fallen to about one-half. In the case of the $^1/_{40}$ normal potassium hydroxide the evidence is not so clear as the experiment was interrupted too soon. One experiment was made with a solution which was $^1/_{26,000,000}$ molar as to brucine hydrochloride. This is here given as Table VIII.

TABLE VIII.

T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	50.00	....	0	48.30	....
1	49.55	0.45	1	47.85	0.45
2	49.15	0.40	2	47.50	0.35
3	48.75	0.40	3	47.18	0.32
4	48.35	0.40	4	46.90	0.28
			5	46.68	0.22
			6	46.45	0.22
			7	46.23	0.21
			8	46.02	0.17
			9	45.85	0.15
			10	45.70	0.17

This, as will be seen, also gives positive evidence of inhibition. But the question arises as to what extent, with ordinary distilled water, inhibition might occur without the addition of brucine and owing solely to some impurity of the water itself or of the salt. To throw some light upon this point a number of observations were made in which no brucine or other substance was added and in which the experiment was continued until about one-half of the sulphite was oxidized. These gave roughly concordant results. One such set is given here:

TABLE IX.

T.	V.	$\frac{\Delta V}{\Delta T}$.	T.	V.	$\frac{\Delta V}{\Delta T}$.
0	44.00	....	11	38.20	0.32
1	43.20	0.80	12	37.90	0.30
2	42.50	0.70	13	37.62	0.28
3	41.82	0.68	14	37.32	0.30
4	41.24	0.58	15	37.10	0.22
5	40.70	0.54	16	36.88	0,22
6	40.15	0.55	17	36.65	0.23
7	39.70	0.45	18	36.42	0.23
8	39.30	0.40	19	36.26	0.16
9	38.90	0.40	20	36.10	0.16
10	38.52	0.38			

From this it will be seen that after one-half (about 7 cc.) of the requisite amount of oxygen for complete oxidation had been absorbed, the rate had fallen to about one-fourth of the original, thus giving some evidence of inhibition. And it may be added that this inhibition, although not quite so large as with $^1/_{26.000.000}$ brucine hydrochloride, is not with any great degree of certainty to be distinguished from it. Thus it is safe to say that the inhi-

bition by brucine hydrochloride becomes practically indistinguishable from accidental inhibition somewhere between $^1/_{2,600,000}$ and $^1/_{26,000,000}$ molar concentration.

Attention is to be called, in passing, to the development period of the inhibition. With very dilute brucine hydrochloride the rate immediately after adding the reagent is almost as large and sometimes larger than before the addition. The rate then falls off more or less rapidly to a minimum. This, as will be seen later, is a very general phenomenon, and a separate investigation will be devoted to it. Also there is to be noted here the very common occurrence of an initial acceleration upon addition of the brucine hydrochloride. This will also be specially investigated.

3. In Acid Solution.—In carrying out the investigation in acid solution a somewhat different method was used. On this account and because the results are of a somewhat different character from the above all studies in acid solution will be brought together under one head at some later time.

B. Experiments with Quinine Bisulphate.

1. In Neutral Solution.—These experiments, as well as those in alkaline solution, were carried out exactly as were those with brucine hydrochloride.

TABLE X.—$^1/_{260}$ MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.18	0.82
	After.	
0	44.10	...
1	43.70	0.40
2	43.22	0.48
3	42.70	0.52
4	42.16	0.54
5	41.62	0.54
6	41.10	0.52
7	40.64	0.46
8	40.18	0.46
9	39.75	0.43
10	39.30	0.45

TABLE XI.—$^1/_{2,600}$ MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.19	0.81
	After.	
0	44.00	...
1	43.62	0.38
2	43.20	0.42
3	42.75	0.45
4	42.30	0.45
5	41.84	0.46
10	39.84	0.40
15	38.70	0.23
20	38.15	0.11
30	37.65	0.05
40	37.33	0.023
50	37.15	0.018

TABLE XII.—$^1/_{26,000}$ MOLAR QUININE BISULPHATE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.05	0.95
	After.	
0	44.20	...
1	43.05	1.15
2	41.75	1.30
3	40.70	1.05
4	39.55	1.15
5	38.25	1.30
10	34.50	0.75
15	34.03	0.094
20	33.94	0.018

TABLE XIII.—$^1/_{260,000}$ MOLAR QUININE BISULPHATE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.20	0.80
	After.	
0	44.20	...
1	43.10	1.10
2	41.90	1.20
3	40.83	1.07
4	39.90	0.93
5	39.10	0.80
10	34.35	0.95
15	33.48	0.18

TABLE XIV.—$^1/_{2,600,000}$ MOLAR QUININE BISULPHATE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	44.13	0.87
	After.	
0	44.10	...
1	43.30	0.80
2	42.48	0.82
3	41.72	0.76
4	41.00	0.72
5	40.28	0.72
10	36.95	0.666
15	35.15	0.36

An examination of these results shows that in dilutions as great as $^1/_{2,600}$ molar, quinine bisulphate shows very distinct inhibitive action. In $^1/_{26,000}$ molar concentration, a distinct initial acceleration is noticed which, however, goes over later into an inhibitive effect. This is more marked when the full set of values per minute is seen, although quite apparent from the abridged table (XII) given here. In Table XIII ($^1/_{260,000}$ molar quinine sulphate), the same acceleration is noticed, while (especially when the table is seen in full) the inhibition is not distinct. In $^1/_{2,600,000}$ molar concentration, the reaction conducts itself as about normal; neither initial acceleration nor inhibition beyond what might be due to the water are apparent. In comparison with brucine hydrochloride, quinine bisulphate acts inhibitively to about the same dilution but shows noticeable initial acceleration, which was not noticed with brucine hydrochloride in neutral solution. The fact that in high concentrations quinine bisulphate does not act so powerfully as brucine hydrochloride, may possibly be

wholly explainable by the formation of the insoluble compound referred to above.

2. In Alkaline Solution.—The following tables (XV to XVIII) show the influence of quinine sulphate in alkaline solution. The solutions used were always 0.1 normal in potassium hydroxide.

TABLE XV.—$^1/_{2,600}$ MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.65	1.35
	After.	
0	43.50	....
1	43.40	0.10
2	43.40	0.00
3	43.40	0.00
4	43.40	0.00

TABLE XVI.—$^1/_{26,000}$ MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.55	1.45
	After.	
0	43.50	....
1	43.30	0.20
2	43.20	0.10
7	42.90	0.06
12	42.77	0.026

TABLE XVII.—$^1/_{260,000}$ MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	44.06	0.94
	After.	
0	43.90	....
1	42.90	1.00
2	42.33	0.57
7	41.17	0.23
12	40.45	0.14

TABLE XVIII.—$^1/_{2,600,000}$ MOLAR QUININE BISULPHATE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.50	1.50
	After.	
0	44.00	....
1	42.40	1.60
2	41.50	0.90
5	40.08	0.49
10	38.75	0.27
15	38.00	0.15

The result here is wholly comparable to that found for brucine hydrochloride. Out to a dilution of $^1/_{260,000}$ molar the inhibitive action is undoubted. At $^1/_{2,600,000}$ molar, inhibition also seems undoubtedly present and that in much higher degree than that usually shown by solutions in ordinary distilled water without any addition of foreign substances (see Table IX).

C. Experiments with Morphine Hydrochloride.

Beginning with the morphine hydrochloride the remainder of the measurements given under this section of the work were carried out in a somewhat different manner; namely, the normal rate without addition was first determined, then the foreign sub-

stance injected in the desired quantity and the rate noted, this giving the inhibition in neutral solution, while finally, the further injection of 1 cc. of a normal potassium hydroxide solution and the further determination of the rate gave the result in alkaline solution. All such solutions were thus $^1/_{27}$ normal in potassium hydroxide. The slight change in the concentration of the inhibitive agent may be neglected for present purposes.

This method of procedure has a great advantage over the older one, in point of time saved, while it has the disadvantage of not allowing one to follow the development of the inhibition very far in neutral solution, especially at considerable dilutions, as were this done, the solution would become so far oxidized that the results in alkaline solution might be uncertain. However, as the whole matter of the development period is to be made the subject of special treatment, no particular harm will result.

The following tables (XIX to XXII) give the results with morphine hydrochloride.

TABLE XIX.—$^1/_{260}$ MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.98	1.02
	After.	
0	44.00	...
1	43.94	0.06
2	43.88	0.06
3	43.82	0.06
4	43.76	0.06
5	43.70	0.06
10	43.42	0.056
15	43.10	0.060

TABLE XX.—$^1/_{2600}$ MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	42.60	2.40
	After.	
0	42.50	...
1	42.20	0.30
2	41.90	0.30
3	41.62	0.28
4	41.40	0.22
5	41.20	0.20
	Added here 1 cc. normal potassium hydroxide.	
0	41.10	...
1	40.88	0.22
6	40.84	0.008
11	40.80	0.008
16	40.80	0.000

TABLE XXI.—$^1/_{26,000}$ MOLAR MORPHINE HYDROCHLORIDE.

T.	V.	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.70	1.30
	After.	
0	43.50	...
1	42.75	0.75
2	42.02	0.73
	Added here 1 cc. normal potassium hydroxide.	
0	42.00	...
1	41.50	0.50
2	41.08	0.42
3	40.80	0.28
4	40.60	0.20
5	40.42	0.18
10	39.96	0.092
15	39.75	0.04
20	39.70	0.01
30	39.70	0.00

TABLE XXII.—$^1/_{260.000}$ MOLAR MORPHINE HYDROCHLORIDE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.15	1.85
	After.	
0	43.20	...
1	41.35	1.85
	Added here 1 cc. normal potassium hydroxide.	
0	41.20	...
1	39.95	1.20
2	39.40	0.55
3	39.15	0.25
4	38.95	0.20
5	38.80	0.15
10	38.36	0.088
15	38.16	0.040
20	38.10	3.010
30	37.88	0.020
40	37.84	0.004
50	37.84	0.000
24 hrs.	37.84	0.000

D. Experiments with Cane-Sugar.

TABLE XXIII.—$^1/_{260}$ MOLAR CANE-SUGAR.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.35	1.65
	After.	
0	43.20	....
1	42.76	0.44
2	42.46	0.30
3	42.20	0.26
4	41.90	0.30
5	41.63	0.27
10	40.43	0.24
	Added here 1 cc. normal potassium hydroxide.	
0	40.20	....
1	40.20	0.00
5	40.20	0.00
10	40.20	0.00
15	40.20	0.00

TABLE XXIV.—$^1/_{2600}$ MOLAR CANE-SUGAR.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	....
1	43.00	2.00
	After.	
0	43.00	....
1	41.60	1.40
	Added here 1 cc. normal potassium hydroxide.	
0	41.50	....
1	40.80	0.70
2	40.53	0.27
3	40.38	0.15
4	40.33	0.05
5	40.31	0.02
10	40.20	0.02
15	40.20	0.00

TABLE XXV.—$^1/_{26.000}$ MOLAR CANE-SUGAR.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	42.60	2.40
	After.	
0	42.50	...
1	40.70	1.80
	Added here 1 cc. normal potassium hydroxide.	
0	41.00	...
1	39.30	1.70
2	38.60	0.70
3	38.00	0.60
4	37.60	0.40
5	37.25	0.35
10	36.40	0.16
15	36.08	0.064
20	35.89	0.040
24 hrs.	35.40	...
4 days	35.40	...

TABLE XXVI.—$^1/_{260.000}$ MOLAR CANE-SUGAR.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.00	2.00
	After adding 1 cc. normal potassium hydroxide.[1]	
0	42.50	...
1	41.25	1.25
2	40.45	0.80
3	39.85	0.60
4	39.60	0.25
5	39.35	0.25
6	39.20	0.15
7	39.03	0.17
8	38.93	0.10
9	38.85	0.08
10	38.79	0.06

E. Experiments with Ammonium Chloride.

TABLE XXVII.—$^1/_{260}$ MOLAR AMMONIUM CHLORIDE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	42.55	2.45
	After.	
0	42.50	...
1	41.25	1.25
2	39.95	1.30
	Added here 1 cc. normal potassium hydroxide.	
0	39.70	...
5	39.28	0.084
10	39.20	0.016
15	39.10	0.020
20	39.10	0.000
24 hrs.	39.10	0.000

TABLE XXVIII.—$^1/_{2600}$ MOLAR AMMONIUM CHLORIDE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	42.80	2.20
	After.	
0	42.00	...
1	40.60	1.40
	Added here 1 cc. normal potassium hydroxide.	
0	40.30	...
1	39.50	0.80
2	39.35	0.15
3	39.16	0.19
4	39.00	0.16
5	38.85	0.15
10	38.33	0.104
15	38.03	0.060

TABLE XXIX.—$^1/_{26,000}$ MOLAR AMMONIUM CHLORIDE.

$T.$	$V.$	$\frac{\Delta V}{\Delta T}$.
	Before.	
0	45.00	...
1	43.00	2.00
	After adding 1 cc. normal potassium hydroxide.	
0	42.80	...
1	41.10	1.70
2	40.00	1.10
3	39.30	0.70
4	38.80	0.50
5	38.48	0.32
10	37.10	0.275

The results of the investigations with morphine chloride, cane-sugar and ammonium chloride are thus in a general way wholly comparable with those for quinine and brucine salts. Morphine

[1] In this experiment the potassium hydroxide was added at the same time as the inhibitive reagent. The same is true in Table XXIX.

hydrochloride seems somewhat more active in neutral solution than the other substances. The influence of cane-sugar in alkaline solution seems of about the same value as of the alkaloids, being still very distinct at $^1/_{260,000}$ molar. Ammonium chloride exerts an influence in alkaline solution which rapidly weakens with dilution. Its influence seems to be, in $^1/_{2600}$ molar solution, only about as great as that of morphine hydrochloride in a one hundred times more dilute solution; namely, $^1/_{260,000}$ molar.

5. EXPERIMENTS IN ACID SOLUTIONS.

As has been already stated the study of the oxidation rate of sodium sulphite in acid solution, particularly under the influence of such catalytic accelerators as copper and iron salts is rather complicated. A number of interesting and curious phenomena have been noticed but they have not been sufficiently investigated at present to allow of any report being made. The inhibitive action of organic substances is very much smaller than in neutral solution, and from some observations seems to be zero. In the case of stannous chloride, however, as has been shown,[1] the action in acid solution is very marked. These investigations in acid solution will be carried further.

6. DISCUSSION AND SUMMARY.

In the present incomplete state of this investigation there is no object in entering into any extended discussion of the results. From the results already given, however, certain generalizations are possible.

1. Evidence is shown, tending to lead to the conclusion that only oxidations by means of free oxygen are subject to inhibition by small quantities of foreign substances.

2. A considerable number of organic substances not previously studied by Bigelow[2] show inhibitive action in high degree. In view of the great number of most diverse substances of organic nature which have been shown by Bigelow and by me, to possess this power, it seems safe to conclude that probably all organic substances possess it.

3. In addition to organic substances the power has been shown to belong also to potassium cyanide, hydroxylamine and ammonium salts.

[1] This Journal, **23**, 137.
[2] *Loc. cit.*

4. The inhibitive effect has been shown in all cases to be not instantaneous, but to develop somewhat slowly with the oxidation of the solution. Ernst[1] noticed the same phenomenon in studying the influence of foreign substances on the catalytic acceleration of the oxidation of hydrogen by colloidal platinum solution. Bigelow[2] noticed the same depression of the oxidation rate toward the end of the reaction, but ascribed it to other causes.

5. As a very common accompaniment of these phenomena, initial accelerations have been found. It is possible that the method of procedure is alone the cause of these not being observed in all cases.

6. The limit of the dilution at which substances still show inhibitive effects differs for different substances, being in some cases still noticeable at a dilution of $^1/_{2,600,000}$ molar. Investigations are now being carried on whose purpose is to subject these phenomena of development periods and of initial accelerations to a careful study in the hope of finding some simple explanation of them. Until this can be done and the phenomena in question either eliminated or controlled, it is hopeless to attempt any exact quantitative investigation of the subject as a whole.

STANFORD UNIV., CAL.,
January 9, 1902.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF METHYL AND ETHYL ALCOHOLS UPON THE BROMIDES OF CERTAIN PROPENYL COMPOUNDS.

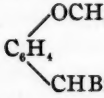
BY F. J. POND, E. S. ERB, AND A. G. FORD.

Received December 21, 1901.

IT has been known for a number of years that certain bromine derivatives of anethol, isosafrol, isoapiol, and other analogous compounds, containing a propenyl group, C_3H_5, joined to a benzene nucleus, dissolve in ethyl alcohol with apparent decomposition, or on boiling with alcohol, they are converted into compounds which contain a less percentage of bromine. Thus Hell and Günthert[3] found that anethol dibromide, $C_{10}H_{12}O.Br_2$, is changed into a dark-colored oil on boiling with absolute alcohol; this oil was not prepared in a chemically pure condition, but on

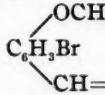
[1] Ernst: *Ztschr. phys. Chem.*, **37**, 478.
[2] *Loc. cit.*
[3] Hell and Günthert: *J. prakt. Chem.*, **52**, 199.

analysis it gave figures indicating the composition $C_{12}H_{17}O_2Br$, and its constitution was represented by the formula



Nothing further appears to have been learned regarding this compound, nor has the action of methyl alcohol on anethol dibromide hitherto been studied.

Also, according to Hell and Günthert,[1] when monobromanethol dibromide, $C_{10}H_{11}OBr.Br_2$, is boiled for some time with absolute ethyl alcohol, ethyl bromide is formed and an oil results which soon solidifies; it separates from ether in crystals melting at 62°. This compound is represented by the formula



and its formation is said to be due to the elimination of 1 molecule of hydrogen bromide from monobromanethol dibromide by means of ethyl alcohol; that is, when anethol dibromide is heated with ethyl alcohol, hydrobromic acid is eliminated and the elements of ethyl alcohol are added, while with the tribromide, hydrogen bromide is given off and an unsaturated bromide, $C_{10}H_{10}OBr_2$, is obtained. The action of methyl alcohol upon the tribromide does not appear to have been investigated.

No definite chemical compounds have been obtained by the action of methyl or ethyl alcohol upon the bromides of other propenyl compounds, although several cases are noted in the literature in which the action of alcohol seems to give rise to non-characteristic oils. For example, Ciamician and Silber[2] found that monobromisosafrol dibromide is changed by the action of boiling ethyl alcohol; they refer to this reaction in the following words: "Mit Wasser oder namentlich mit Alkohol gekocht scheint es Bromwasserstoff abzuspalten." Hell and Hoering[3] state that a non-characteristic oil is formed when monobromisosafrol dibromide is boiled with ethyl alcohol: "Mit Alkohol erhitz gaben die Krystalle eine Schmiere, woraus keine Krystalle mehr zu erhalten waren."

[1] Hell and Günthert: *J. prakt. Chem.*, **52**, 199.
[2] Ciamician and Silber: *Ber. d. chem. Ges.*, **23**, 1164.
[3] Hoering: *Inaug. Diss.* (Rostock), p. 59 (1897).

The fact that anisylidene acetophenone dibromide is converted by boiling ethyl alcohol into a definite and crystalline ethyl alcohol addition-product of monobromanisylidene acetophenone,[1] and by methyl alcohol into a corresponding, higher melting methyl alcohol addition-product, led to the belief that similar changes take place when the bromides of certain propenyl compounds are boiled with alcohols. This belief has been justified by the preparation of several characteristic alcohol addition-products.

In our experimental work we have succeeded in preparing the methyl and ethyl alcohol addition-products of monobromanethol by boiling anethol dibromide with the corresponding alcohols. Both compounds are liquids, and are converted into anisyl ethyl ketone,[2] $C_{10}H_{12}O_2$, on treatment with *one* molecular proportion of sodium methylate or alcoholic potash; this ketone was first prepared by Wallach and Pond by treating anethol dibromide with *two* molecules of sodium methylate.

It has been found that when monobromanethol dibromide is boiled with, or crystallized from, methyl alcohol, it is converted into the methyl alcohol addition-product,

$$C_6H_3Br\begin{cases}OCH_3\\ CH(OCH_3)—CHBr—CH_3\end{cases}$$

This substance forms large, magnificent crystals, which melt at 72°–74°. The corresponding ethyl alcohol addition-product is an oil. When these compounds are treated with *one* molecule of sodium alcoholate or alcoholic potash and the resulting product is hydrolyzed with hydrochloric acid, monobromanisyl ethyl ketone,

$$C_6H_3Br\begin{cases}OCH_3\\ CO—CH_2—CH_3\end{cases},$$

is obtained. This ketone forms long needles, melts at 100°, and was first prepared by Hell and Hollenberg[3] by the action of *two* molecules of sodium alcoholate upon monobromanethol dibromide.

Two new compounds are obtained by the action of methyl and

[1] Pond and Shoffstall: This Journal, **22**, 668 and 670.

[2] Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2715; see also Hell and Hollenberg: *Ibid.*, **29**, 687.

[3] Hell and Hollenberg: *Ber. d. chem. Ges.*, **29**, 686; See Hell and Gärttner: *J. prakt. Chem.*, **51**, 428.

ethyl alcohol on monobromisosafrol dibromide, $C_{10}H_9O_2Br.Br_2$; the methyl alcohol product separates in well-formed crystals, and melts at 75°–76°, and the ethyl alcohol compound forms large crystals, melting at 59°–60°. The corresponding monobromoketone, $C_{10}H_9O_3Br$, has not been obtained.

Ethylisoeugenol dibromide, $C_{12}H_{16}O_2.Br_2$, is also changed by boiling with methyl and ethyl alcohol; the former gives rise to a crystalline compound melting at 68°, while the latter yields an oil.

Monobromisoapiol dibromide, $C_{12}H_{13}O_4Br.Br_2$, is converted into a crystalline product on boiling with methyl alcohol; it melts at 92°. The ethyl alcohol addition-product is an oil.

The reaction by which these various alcohol addition-products are formed, is probably to be represented by the following equation:

$$R—CHBr—CHBr—CH_3 + CH_3OH = HBr + R—CH(OCH_3)—CHBr—CH_3 \text{ or } R—CHBr—CH(OCH_3)—CH_3.$$

I. II.

For the present we prefer to represent the alcohol addition-products by the general formula I. This formula more readily explains the formation of ketones,

$$R—CO—CH_2—CH_3,$$

by the action of *one* molecular proportion of sodium alcoholate or alcoholic potash:

1. $R—CH(OCH_3)—CHBr—CH_3 + KOH = R—C(OCH_3)=CH—CH_3 + KBr + H_2O.$
2. $R—C(OCH_3)=CH—CH_3 + H_2O = R—C(OH)=CH—CH_3 + CH_3OH.$
3. $R—C(OH)=CH—CH_3 = R—CO—CH_2—CH_3.$

It has previously[1] been proved that these ketones contain the carbonyl group in the α-position to the benzene ring.

If formula II be accepted for these alcohol additive compounds, it would be expected that alcoholic potash would eliminate hydrogen bromide with the ultimate formation of isomeric ketones,

$$R—CH_2—CO—CH_3;$$

this, however, is not apparently the case.

Owing to the limited time for our work, the investigation of the compounds which are mentioned in the following pages, is

[1] Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2718; see also Hell and Hollenberg: *Ibid.*, **29**, 688.

very far from complete, but we deem it desirable to publish the results obtained at this time with the view of reserving this line of research. During the current year we propose to continue these investigations and to extend them to some other propenyl compounds.

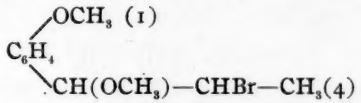
EXPERIMENTAL.

Anethol Dibromide, $C_6H_4(OCH_3).C_3H_5Br_2$, was prepared according to Ladenburg's method.[1]

Forty grams of anethol were dissolved in 200 cc. of ether, and the solution was well cooled with a freezing-mixture; one molecular proportion (43.2 grams) of bromine was added very slowly and with constant shaking. The slight excess of bromine was then removed by shaking the ethereal solution with sulphurous acid, and the ether allowed to evaporate slowly; the resulting crystalline mass was recrystallized from petroleum ether, yielding white needles, which melted at 62°–64°.

The Action of Methyl Alcohol upon Anethol Dibromide.

Methyl Alcohol Addition-Product of Monobromanethol,



A solution of 30 grams of anethol dibromide in 90 cc. of methyl alcohol was boiled for one hour in a reflux apparatus; the solution at first assumed a light pink color, but darkened as the boiling continued. On completion of the reaction the liquid reacted acid, due to the elimination of hydrobromic acid. The contents of the flask were then poured into a large quantity of cold water, and the resulting oil was separated, washed with water and extracted with ether; the ethereal solution was repeatedly shaken with water, dried over anhydrous sodium sulphate, and the ether evaporated. A mobile oil resulted, which had a light yellow color, and was decomposed on distillation. It dissolves readily in alcohol, ether, chloroform and acetic acid, but could not be obtained in a crystalline form. The bromine determination gave:

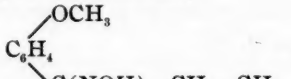
[1] Ladenburg: *Ann. Chem.* (Liebig), Suppl., **8**, 94; *Ber. d. chem. Ges.*, **2**, 372.

I. 0.2029 gram gave 0.1456 gram silver bromide.
II. 0.2027 gram gave 0.1447 gram silver bromide.

	Calculated for $C_{11}H_{15}O_2Br$.	Found. I.	II.
Bromine	30.88	30.54	30.37

When this oil is treated with one molecular proportion of sodium alcoholate and the resulting product is boiled with hydrochloric acid, anisyl ethyl ketone, $C_{10}H_{12}O_2$, is obtained.

Forty-four grams of the methyl alcohol addition-product of bromanethol were added to a solution of one molecule of sodium methylate (4 grams of sodium in 100 cc. of methyl alcohol), and boiled for four hours. At the end of this time, the liquid reacted slightly alkaline, and contained considerable sodium bromide. Sufficient water was added to dissolve the sodium bromide and to precipitate the resulting oil. The latter was separated and warmed for about fifteen minutes with dilute hydrochloric acid; it was then distilled with steam. An almost colorless oil was obtained, which, on treatment with hydroxylamine, was converted into a solid oxime. The oxime crystallized from alcohol-ether in large prisms, melting at 73°–74°; it is identical in all respects with anisyl ethyl ketoxime,



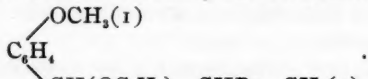
which Wallach and Pond[1] obtained from the oil resulting on the treatment of anethol dibromide with *two* molecules of sodium methylate. On treating this oxime with dilute sulphuric acid, anisyl ethyl ketone (m. p. 26°–27°) was formed.

The same oxime (m. p. 74°) was also obtained by a similar treatment of the methyl alcohol addition-product of monobromanethol with one molecule of sodium ethylate and alcoholic potassium hydroxide.

The yield of anisyl ethyl ketone by this method of preparation is better than by the direct action of two molecules of sodium methylate on anethol dibromide.

The Action of Ethyl Alcohol upon Anethol Dibromide.

Ethyl Alcohol Addition-Product of Monobromanethol,



[1] Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2715.

It was mentioned in the introduction that Hell and Günthert[1] studied this reaction. They found that boiling ethyl alcohol converts anethol dibromide into a dark brown, resinous mass which possesses a strong anethol-like odor; it dissolves in ether, alcohol, benzene, chloroform, and acetic acid. Analysis of this oil gave 28.57 per cent. of bromine, and from this it was regarded that the oil was the ethyl alcohol addition-product of monobromanethol, $C_{12}H_{17}O_2Br$.

The results of our investigation fully confirm this view. Thirty grams of anethol dibromide were boiled with 90 cc. of ethyl alcohol for one hour, and the reaction-product was poured into cold water. The resulting dark-colored oil was washed repeatedly with water, extracted with ether, again washed, and dried over anhydrous sodium sulphate. On evaporation of the ether, a dark, rather mobile oil resulted; it could not be purified by distillation, but on analysis gave the following results:

I. 0.2020 gram gave 0.1398 gram silver bromide.
II. 0.2028 gram gave 0.1399 gram silver bromide.

	Calculated for $C_{12}H_{17}O_2Br$.	Found. I.	II.
Bromine.....	29.30	29.45	29.35

This compound was also readily converted into anisyl ethyl ketone, $C_{10}H_{12}O_2$, by the action of sodium alcoholate or alcoholic potash; its oxime melted at 72°–74°.

Monobromanethol Dibromide,

$$C_6H_3Br\begin{cases} OCH_3(1) \\ CHBr—CHBr—CH_3(4) \end{cases}$$

This compound was first prepared by Cahours[2] by the addition of bromine to anethol; he regarded it as tribromanethol, $C_{10}H_9Br_3O$. In 1895, Hell and Gärttner[3] obtained it by adding slowly to a cold, ethereal solution of anethol, the calculated amount of bromine (two molecules). We have found the following method to be the most satisfactory for the preparation of large quantities of the substance.

To a solution of 100 grams of anethol in 75 cc. of ether, 216.2 grams (2 molecules) of bromine are added quite rapidly, the flask

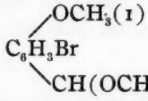
[1] Hell and Günthert: *J. prakt. Chem.*, **52**, 199.
[2] Cahours: *Ann. Chem.* (Liebig), **41**, 60.
[3] Hell and Gärttner: *J. prakt. Chem.*, **51**, 425; **52**, 193; see also Orndorff and Morton: *Am. Chem. J.*, **23**, 185.

in which the bromination is carried on being placed in ordinary cold water; an especially low temperature and a gradual addition of the bromine are not only unnecessary, but retard the process. When the addition of bromine is complete, the black, oily product is poured into an open dish and allowed to stand, or may be stirred for a few minutes; the product then solidifies with violent evolution of hydrogen bromide. It is now placed on a suction filter, washed very sparingly with ether, and then spread out on a large filter-paper. After twelve hours, it is again washed on a suction filter with a little ether until it assumes a permanent white color. This product melts at 108°–112°, and is quite pure; it was used in the following described experiments.

Orndorff and Morton[1] purified this compound by dissolving it in a small amount of chloroform and then precipitating with ethyl alcohol. Our experience has been that, although this method gives a pure, crystalline product, a large quantity of the substance suffers decomposition by such treatment, doubtless due to the action of the alcohol.

The Action of Methyl Alcohol upon Monobromanethol Dibromide.

Methyl Alcohol Addition-Product of Dibromanethol,



—Thirty grams of monobromanethol dibromide were dissolved in 100 cc. of methyl alcohol in a flask fitted with a reflux condenser and boiled for two hours on a steam-bath. The resulting, slightly yellow colored solution had an acid reaction, and gave off fumes of hydrobromic acid; it was poured into a beaker and allowed to stand. In a few hours crystals separated, which were removed and recrystallized from acetone; beautiful, large, colorless prisms resulted, which melted at 71°–74°.

In another preparation, 135 grams of monobromanethol dibromide were boiled with 380 cc. of methyl alcohol for one hour, the slightly colored solution was filtered and allowed to crystallize. The resultant crystals were repeatedly crystallized from methyl alcohol and finally obtained in large, colorless prisms, melting at 73°–74°.

It was further learned that the same compound may be readily

[1] Orndorff and Morton: *Am. Chem. J.*, **23**, 185.

obtained by dissolving monobromanethol dibromide in methyl alcohol in a beaker, heating the solution to the boiling-point, and allowing to crystallize; on recrystallization from methyl alcohol, the compound is obtained pure and melts at 73°–74°.

Analyses gave the following results:[1]

I. 0.2052 gram gave 0.2952 gram carbon dioxide and 0.0816 gram water.
II. 0.3000 gram gave 0.4308 gram carbon dioxide and 0.1114 gram water.
III. 0.2128 gram gave 0.2378 gram silver bromide.
IV. 0.2128 gram gave 0.2380 gram silver bromide.

	Calculated for $C_{11}H_{14}O_2Br_2$.	Found. I.	II.	III.	IV.
Carbon	39.05	39.23	39.16	....	....
Hydrogen	4.14	4.42	4.12	....	....
Bromine	47.34	....	....	47.55	47.59

This compound is readily soluble in the usual organic solvents, and may be recrystallized, without change, from boiling ethyl alcohol. On distillation under a pressure of 14 to 15 mm., it boils without decomposition at 160°–164° yielding a colorless and odorless oil, which solidifies after standing a few hours, and again melts at 72°–74°; if the pressure be slightly increased, the compound suffers some decomposition with evolution of hydrogen bromide, and the distillate does not become solid.

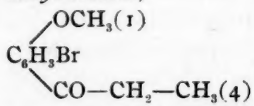
When the compound was heated carefully at the atmospheric pressure, it melted to a colorless liquid; at 130°, the liquid assumed a yellowish color, which rapidly became darker as the temperature increased. From 170°–195°, a colorless liquid distilled over and was proved to be methyl alcohol. At 195°, the heat was removed, and on cooling, the contents of the flask appeared as a black thick oil, which did not solidify after standing for several months.

It reacts as a saturated compound, since it does not decolorize permanganate and its ethereal solution does not absorb bromine.

An attempt was made to remove the elements of hydrogen bromide by boiling a solution of 20 grams of the compound in 100 cc. of methyl alcohol with 4 grams of anhydrous sodium acetate for twelve hours, but after filtering the reaction-product, the unchanged substance was obtained and melted at 72°–73°. Hydrobromic acid may be readily removed, however, by the action of sodium alcoholate or alcoholic potash.

[1] These analyses were made by Mr. C. R. Siegfried, to whom we wish here to express our thanks.

Monobromanisyl Ethyl Ketone,



—Ten grams of the methyl alcohol addition-product of dibromanethol, $C_{11}H_{14}O_2Br_2$, were added to a solution of one molecule of sodium methylate (0.8 gram of sodium in 25 cc. of methyl alcohol), and boiled for two hours. At the end of this time sodium bromide had separated and the liquid reacted slightly alkaline; water was added and the liquid was made slightly acid with hydrochloric acid, when a colorless oil, heavier than water, separated. The aqueous, alcoholic liquid was decanted, and the oil treated with concentrated hydrochloric acid; after stirring for a few seconds, the oil was completely converted into a white solid. The latter was washed free from acid and crystallized from alcohol; it separated in beautiful, long needles, which melted at 100°–101°.

Analyses gave the following results:

I. 0.3000 gram gave 0.5403 gram carbon dioxide and 0.1364 gram water.
II. 0.2008 gram gave 0.1549 gram silver bromide.
III. 0.2000 gram gave 0.1549 gram silver bromide.

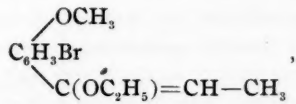
	Calculated for $C_{10}H_{11}BrO_2$.	Found. I.	II.	III.
Carbon	49.38	49.11	....	....
Hydrogen	4.53	5.05	....	....
Bromine	32.92	....	32.82	32.95

The formation of this ketone is to be explained by the fact that sodium methylate removes one molecule of hydrogen bromide yielding an unsaturated ether; the latter is hydrolyzed by hydrochloric acid, and the resulting unsaturated alcohol suffers an intramolecular change into the more stable, saturated ketone.

The same ketone (m. p., 100°) is also formed by the action of one molecule of potassium hydroxide, dissolved in alcohol, on the methyl alcohol addition-product, and subsequent treatment with hydrochloric acid.

This ketone was prepared by Hell and Hollenberg[1] by the action of two molecules of sodium ethylate upon one molecular proportion of monobromanethol dibromide; they also isolated the unsaturated ether,

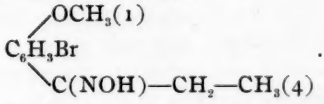
[1] Hell and Hollenberg: *Ber. d. chem. Ges.*, **29**, 683; see also Hell and Gärttner: *J. prakt. Chem.*, **51**, 424.



which is an oil boiling at 180°–182° (16 mm.), but they did not obtain the first reaction-product, *viz.*, the alcohol addition-product.

To further characterize this ketone, we have converted it into the oxime.

Monobromanisyl Ethyl Ketoxime,



—Ten grams of the ketone were dissolved in alcohol and treated in the usual manner with hydroxylamine; on precipitating the reaction-product with water, an oil resulted which soon solidified. It was crystallized from alcohol and separated in splendid crystals, melting at 108°.

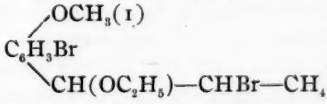
On analysis, it gave the following results for bromine:

I. 0.2004 gram gave 0.1464 gram silver bromide.
II. 0.2003 gram gave 0.1457 gram silver bromide.

	Calculated for $C_{10}H_{12}O_2BrN$.	Found. I.	II.
Bromine	31.01	31.08	30.95

The Action of Ethyl Alcohol upon Monobromanethol Dibromide.

Ethyl Alcohol Addition-Product of Dibromanethol,



A solution of 20 grams of monobromanethol dibromide in 50 cc. of absolute ethyl alcohol was boiled for three minutes on a water-bath; on evaporation of the alcohol, an oil resulted, which was washed with water, extracted with ether, and dried over anhydrous sodium sulphate. After evaporation of the ether over fused calcium chloride in vacuum, a mobile, amber-colored oil was obtained, which gave the following figures on analysis:

I. 0.2021 gram gave 0.2161 gram silver bromide.
II. 0.2012 gram gave 0.2153 gram silver bromide.

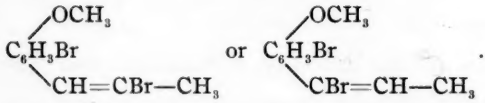
	Calculated for $C_{12}H_{16}O_2Br_2$.	Found. I.	II.
Bromine	45.45	45.50	45.53

This compound could not be obtained in a solid condition. The same oil was found in a number of other experiments in which different proportions of alcohol were used, and the boiling was carried on for various lengths of time, from four minutes to three hours.

On heating this oil in a flask to 196° under atmospheric pressure, ethyl alcohol is given off and is recognized by the iodoform reaction. The oil does not reduce permanganate in the cold, and its ethereal solution absorbs no bromine.

When this oil is treated with one molecular proportion of sodium alcoholate or alcoholic potash, and then with concentrated hydrochloric acid, it is readily and quantitatively converted into monobromanisyl ethyl ketone, melting at 99°–100°.

According to Hell and Günthert,[1] when monobromanethol dibromide is boiled with absolute ethyl alcohol for twenty-four hours and the alcohol is then distilled off, ethyl bromide is formed and an oil results which gradually solidifies after pouring into cold water; it crystallizes from ether in long, prismatic crystals which melt at 62°. On analysis this compound gave results indicating the formula $C_{10}H_{10}Br_2O$, and Hell regards it as an unsaturated bromide,



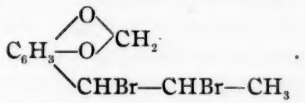
On repeating this experiment, following as closely as possible the directions indicated by Hell, we were unable to obtain the substance in a solid form until the oil had remained for several hours at a temperature below 0°. By this method, a small proportion of the oil gradually became solid and, after recrystallization from ether, melted at 64°–66°; most of the reaction-product remained as an oil which consisted largely of the ethyl alcohol addition-product above mentioned.

It appears, therefore, that the reaction may take place in two ways, depending on the time that the bromide is heated with the alcohol, and on the subsequent treatment, as the removal of alcohol by gradual evaporation at the ordinary temperature or by distillation; by the former treatment, a product consisting almost entirely of the liquid addition-product results, while the latter

[1] Hell and Günthert: *J. prakt. Chem.*, **52**, 199.

method yields some of the solid, unsaturated bromide, together with considerable liquid addition-product.

Isosafrol Dibromide,



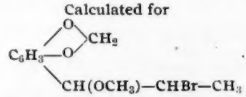
—The isosafrol necessary for our work was prepared from safrol according to the method of Eykman.[1] It was readily converted into the dibromide[2] by the gradual addition of one molecule of bromine to its cold, ethereal solution. The dibromide remained as a colorless oil after evaporation of the ether.

The Action of Methyl and Ethyl Alcohols upon Isosafrol Dibromide.

These reactions were carried on in a manner similar to that mentioned under anethol dibromide by boiling about 50 grams of the dibromide with 150 cc. of the alcohol for one hour. In this case, oils were formed which could not be obtained in a pure condition. Bromine analyses were made of the crude oils, which were purified as carefully as possible. The results are as follows :

1. Oil resulting by boiling isosafrol dibromide with methyl alcohol.

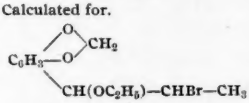
I. 0.2024 gram gave 0.1452 gram silver bromide.
II. 0.2029 gram gave 0.1465 gram silver bromide.



	Calculated	Found. I.	II.
Bromine.....	29.30	30.52	31.09

2. Oil resulting by boiling isosafrol dibromide with ethyl alcohol.

I. 0.2017 gram gave 0.1388 gram silver bromide.
II. 0.2005 gram gave 0.1376 gram silver bromide.

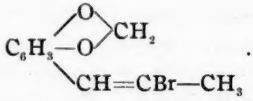


	Calculated	Found. I.	II.
Bromine.....	27.87	29.28	29.20

[1] Eykman : *Ber. d. chem. Ges.*, **23**, 855: Ciamician and Silber : *Ibid.*, **23**, 1159: Angeli : *Gazz. chim. ital.*, (2) **23**, 101.

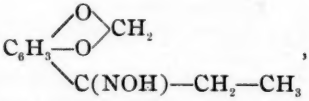
[2] Wallach and Pond : *Ber. d. chem. Ges.*, **28**, 2719.

These analyses are, of course, of no value in determining the exact constitution of the two compounds under consideration, but they indicate that the oils are the methyl and ethyl alcohol addition-products of monobromisosafrol; for if the action of the alcohols caused the elimination of hydrogen bromide without the addition of the elements of the alcohols, it should give rise, in both cases, to the same compound, monobromisosafrol,



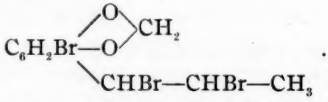
This compound would demand 33.19 per cent. of bromine, which is considerably in excess of that found. In the near future, we hope to obtain these two compounds in a pure condition.

Another circumstance which inclines us to the view that the two oils are alcohol addition-products of monobromisosafrol is the behavior of the methyl alcohol product towards sodium alcoholate. When it is boiled with one molecule of sodium alcoholate or alcoholic potash, and the resulting product is treated as usual with hydrochloric acid, a liquid is obtained, which yields an oxime on treatment with hydroxylamine; this oxime crystallizes from alcohol in short prisms, melts at 101°–102°, and is identical with the oxime[1]



which is produced from the compound resulting by the treatment of isosafrol dibromide with two molecules of sodium methylate.

Monobromisosafrol Dibromide,



—This compound was first prepared by Ciamician and Silber[2] by adding an excess of bromine to a solution of isosafrol in carbon bisulphide, and then heating for a considerable time in a reflux apparatus. It was subsequently obtained by Hell and Hoering[3]

[1] Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2719.
[2] Ciamician and Silber: *Ibid.*, **23**, 1163.
[3] Hoering: Inaug. Diss. (Rostock), p. 58, (1897).

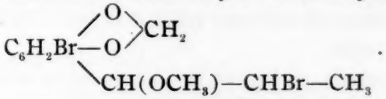
by slowly adding two molecules of bromine to an ethereal solution of isosafrol; the product was recrystallized from petroleum ether, and melted at 109.5°.

We find the following method well adapted for the preparation of this compound.

Thirty grams of isosafrol are dissolved in 90 cc. of ether, and 59.3 grams (2 molecules) of bromine are added as rapidly as the reaction will permit, without cooling. The dark-colored reaction-product is allowed to stand in an open vessel until the ether evaporates, when the substance remains as a crystalline mass. It is filtered by suction, washed with a little ether and then with a small quantity of cold alcohol, and crystallized from ethyl acetate; the crystals melt at 110°–111°. It also crystallizes in large, colorless prisms from a solution in acetone to which an equal volume of ether is added.

The Action of Methyl Alcohol upon Monobromisosafrol Dibromide.

Methyl Alcohol Addition-Product of Dibromisosafrol,



—Thirty grams of monobromisosafrol dibromide were dissolved in 80 cc. of methyl alcohol and boiled with reflux condenser on the steam-bath for about two hours. The solution became slightly colored and gave an acid reaction; hydrobromic acid was given off. The reaction-product was poured into a beaker and the alcohol allowed to evaporate; the residue consisted of a light-colored, heavy oil, which solidified to a white mass after standing during several days. It was subsequently learned that the same solid compound is more readily formed by boiling the methyl alcoholic solution of the tribromide for about three minutes, and then adding a small quantity of water to the solution; the compound is then precipitated *at once* in fine crystals.

It is recrystallized from methyl alcohol; it separates from a concentrated solution in very fine needles, but from dilute solutions in large, prismatic crystals; both forms of crystals melt at 75°–76.5°. It may be recrystallized without change from ethyl alcohol.

It was analyzed with the following results:[1]

[1] These analyses were made by Mr. C. R. Siegfried, to whom we wish here to express our thanks.

I. 0.2118 gram gave 0.2905 gram carbon dioxide and 0.0693 gram water.
II. 0.1916 gram gave 0.2634 gram carbon dioxide and 0.0615 gram water.
III. 0.2204 gram gave 0.2380 gram silver bromide.
IV. 0.2204 gram gave 0.2382 gram silver bromide.

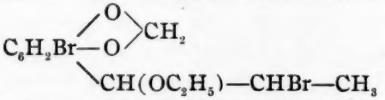
	Calculated for $C_{11}H_{12}O_3Br_2$.	Found. I.	II.	III.	IV.
Carbon	37.50	37.40	37.49	....	....
Hydrogen	3.41	3.63	3.56	....	....
Bromine	45.45	....	....	45.94	45.98

Although the corresponding methyl alcohol addition-product of dibromanethol is very readily converted into a ketone by treatment with one molecule of sodium alcoholate or alcoholic potash, no such change appears to take place with this isosafrol derivative. When 10 grams of the compound were heated with an excess of sodium methylate on the steam-bath for twenty-four hours, no reaction took place. The mixture was then heated in an oil-bath at a temperature of 150° until most of the excess of alcohol was removed; no sodium bromide was eliminated and, on the addition of water, an oil separated which soon solidified; this crystallized from alcohol and melted at 76°, indicating the unchanged compound.

Alcoholic potash, and even the action of an excess of metallic sodium on the alcoholic solution of the compound do not remove hydrogen bromide from this substance.

The Action of Ethyl Alcohol upon Monobromisosafrol Dibromide.

Ethyl Alcohol Addition-Product of Dibromisosafrol,



—It has already been mentioned that Hell and Hoering[1] have reported on this action; they state that when monobromisosafrol dibromide is boiled with alcohol, it yields a non-characteristic oil ("Schmiere") from which no crystalline compound is to be obtained. The results of our experiments do not quite confirm these observations.

When 30 grams of the tribromide were boiled with 80 cc. of absolute ethyl alcohol for about two hours, and the alcohol was then allowed to evaporate, a light-colored, heavy oil separated, which became solid after standing two weeks. It crystallized

[1] Hoering: Inaug. Diss. (Rostock), p. 59, (1897).

from an alcoholic solution in beautiful, large, rhombohedral crystals, and melted at 58°–60°. The same compound is more readily formed by dissolving the tribromide in ethyl alcohol, heating to the boiling-point for a few minutes, and then adding a small quantity of water; it then separates *at once* in small crystals, which, on recrystallization from alcohol, yield the large crystals above mentioned.

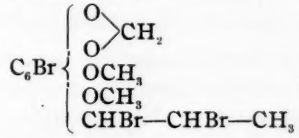
Analysis gave the following:[1]

I. 0.1835 gram gave 0.2650 gram carbon dioxide and 0.0665 gram water.
II. 0.1892 gram gave 0.2686 gram carbon dioxide and 0.0658 gram water.
III. 0.2070 gram gave 0.2130 gram silver bromide.
IV. 0.2070 gram gave 0.2132 gram silver bromide.

	Calculated for $C_{12}H_{14}O_3Br_2$.	Found. I.	II.	III.	IV.
Carbon	39.34	39.38	38.71	....	....
Hydrogen	3.82	4.02	3.86	....	....
Bromine	43.71	....	....	43.78	43.82

When 10 grams of this compound are boiled with an excess of sodium alcoholate, no action appears to take place, the unchanged substance (m. p. 58°–60°) crystallizing from the reaction mixture.

Monobromisoapiol Dibromide,[2]



—The isoapiol,[3] $C_{12}H_{14}O_4$, necessary for our experiments was prepared by boiling apiol with alcoholic potash; it was recrystallized from acetone and melted at 55°–56°.

Monobromisoapiol dibromide was first prepared by Ginsberg[4] by the gradual addition of two parts of bromine dissolved in carbon bisulphide to a solution of one part of isoapiol in the same solvent; it was crystallized from glacial acetic acid and melted at 120°.

We find that it is more readily prepared by dissolving 52 grams of isoapiol in 52 cc. of ether, and adding 27.5 cc. (2 molecules) of bromine to the solution; the addition of the bromine may take place quite rapidly while the solution is cooled by ordinary cold

[1] These analyses were made by Mr. C. R. Siegfried.

[2] Ginsberg: *Ber. d. chem. Ges.*, **21**, 2515.

[3] Ciamician and Silber: *Ber. d. chem. Ges.*, **21**, 1621; Ginsberg: *Ibid.*, **21**, 1192; See also Gerichten: *Ibid.*, **9**, 1479.

[4] *Loc. cit.*

water. The reaction mixture is then placed in a beaker and the ether and hydrogen bromide removed by the aid of a vacuum desiccator. The resulting crystalline mass, which is only slightly colored, is recrystallized from acetone from which it separates in colorless prisms, melting at 120°.

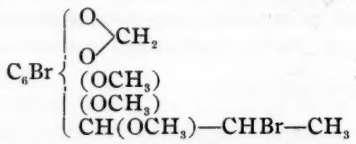
Analyses gave:

I. 0.3000 gram gave 0.3445 gram carbon dioxide and 0.0772 gram water.
II. 0.2000 gram gave 0.2448 gram silver bromide.
III. 0.2010 gram gave 0.2451 gram silver bromide.

	Calculated for $C_{12}H_{18}O_4Br_2$.	Found. I.	II.	III.
Carbon	31.23	31.31	....	....
Hydrogen	2.82	2.86	....	....
Bromine	52.06	....	52.08	51.88

The Action of Methyl Alcohol upon Monobromisoapiol Dibromide.

Methyl Alcohol Addition-Product of Dibromisoapiol,



—This compound is formed by boiling monobromisoapiol dibromide with methyl alcohol for about fifteen minutes and then adding a small quantity of water to the hot solution. It usually separates at once in crystals, but under certain conditions it first forms an oil, which rapidly solidifies. It is recrystallized from methyl alcohol and obtained in large prisms, melting at 92°.

It was analyzed with the following results:

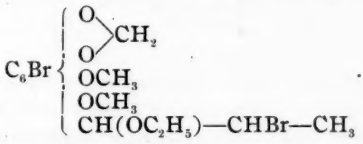
I. 0.3001 gram gave 0.4148 gram carbon dioxide and 0.1069 gram water.
II. 0.3006 gram gave 0.4143 gram carbon dioxide and 0.1092 gram water.
III. 0.2006 gram gave 0.1828 gram silver bromide.
IV. 0.2013 gram gave 0.1838 gram silver bromide.

	Calculated for $C_{13}H_{16}O_5Br_2$.	Found. I.	II.	III.	IV.
Carbon	37.86	37.69	37.58	....	....
Hydrogen	3.88	3.95	4.03	....	....
Bromine	38.83	....	....	38.78	38.85

Sodium alcoholate is apparently without action upon this compound.

The Action of Ethyl Alcohol upon Monobromisoapiol Dibromide.

Ethyl Alcohol Addition-Product of Dibromisoapiol,



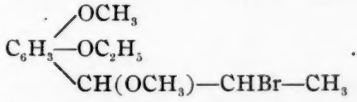
—Monobromisoapiol dibromide was boiled with three times its quantity of ethyl alcohol for about forty-five minutes. The solution had a dark color and an acid reaction; on the addition of water, an oil separated, which was carefully washed with water, extracted with ether and dried. On evaporation of the ether a rather dark-colored, viscous oil resulted, which gave the following results on analysis for bromine:

I. 0.2077 gram gave 0.1805 gram silver bromide.
II. 0.2137 gram gave 0.1840 gram silver bromide.

	Calculated for $C_{14}H_{18}O_5Br_2$.	Found. I.	II.
Bromine	37.56	36.98	36.63

The Action of Methyl Alcohol upon Ethylisoeugenol Dibromide.

Methyl Alcohol Addition-Product of Ethylmonobromisoeugenol,



—Forty grams of ethylisoeugenol dibromide,[1] $C_{12}H_{16}O_2.Br_2$, were boiled with 100 cc. of methyl alcohol for about two hours, and the reaction-product allowed to stand in an open dish until the excess of alcohol evaporated. The residue consisted of an oil which gradually solidified; this was filtered by suction, washed sparingly with cold alcohol, and repeatedly crystallized from ethyl alcohol. It was rather difficult to remove some oily impurities from the compound, but after boiling with animal charcoal, it crystallized from alcohol in large colorless prisms, melting at 68°. It is quite soluble in methyl and ethyl alcohols, ether and acetone.

[1] Wallach and Pond: *Ber. d. chem. Ges.*, **28**, 2720.

Analysis gave the following:

I. 0.2009 gram gave 0.1243 gram silver bromide.
II. 0.2008 gram gave 0.1237 gram silver bromide.

	Calculated for $C_{13}H_{19}O_3Br$.	Found. I.	II.
Bromine.....	26.40	26.32	26.21

It should also be mentioned that in one preparation of this compound by boiling ethylisoeugenol dibromide with methyl alcohol, another compound was formed, together with the methyl alcohol addition-product; it was separated by fractional crystallization from ethyl alcohol in which it is more sparingly soluble than the addition-product. It crystallizes in fine needles and melts at 128°; it contains no bromine, but has not been further investigated.

[CONTRIBUTION FROM THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION. COMMUNICATED BY W. A. WITHERS.]

THE DETERMINATION OF SULPHUR IN PLANTS.

BY G. S. FRAPS.

Received December 5, 1901.

IN a previous issue of this Journal[1] the author called attention to the loss of sulphur in preparing ash of plants. The conclusion reached was that "the sulphur obtained when the ash was burned by itself is from 4 to 100 per cent. less than when burned with calcium acetate. Whether the calcium acetate retains all the sulphur or not, is a point which requires further study." The facts which will be presented here show that the calcium acetate does not retain all the sulphur.

The object of the work was to compare the calcium acetate method with some method by the use of which we could be reasonably certain that all the sulphur contained in the plant in inorganic or organic combination would be retained and determined. A great difficulty is that a very small amount of sulphur is contained in a large quantity of plant material. The Liebig method (fusion with potassium hydroxide and a small amount of potassium nitrate in a silver dish) and the Carius method (heating in a sealed tube with fuming nitric acid) were considered, but offered difficulties on account of the large quantity of organic material to be handled. The following method was finally adopted for trial:

Fifteen grams material were placed in a flat porcelain dish of about 250 cc. capacity, 35 cc. of nitric acid (conc.) added, and the

[1] **23**, 199 (1901).

mixture heated gently until the action had moderated. One gram potassium nitrate was then added, and the mixture evaporated to a thin paste, transferred to a platinum dish, evaporated on a water-bath, and ignited to an ash. After heating for some time, the ash was dissolved in dilute hydrochloric acid, the solution evaporated to dryness, and the residue dried thoroughly to render silica insoluble. It was moistened with a little dilute hydrochloric acid, evaporated, and again dried. The residue was moistened with about 5 cc. of hydrochloric acid, taken up with about 50 cc. of boiling water, filtered, and sulphuric acid determined in the filtrate by the usual method.

A blank determination with the reagents proved them to be free from sulphur. The sulphur (as sulphur trioxide) found by this method compared with the others is given in the following table :

SULPHUR TRIOXIDE IN PLANT (AIR-DRY).

	In ash (usual way). Per cent.	In calcium acetate ash. Per cent.	Nitric acid method. Per cent.
Wheat bran	...	0.221	0.368
Cottonseed meal	...	0.343	0.926
Green rape	1.02	1.25	1.63
Wheat bran	0.00	0.14	0.30
Corn silage.....	0.20	0.24	0.43
Timothy hay	0.15	0.17	0.28

It is evident that the calcium acetate method does not give correct values for sulphur.

It is not believed that the loss of sulphur is due to volatilization of *sulphates*, but to the escape of organic sulphur compounds which are not burned or oxidized. Most of the sulphur in a plant is not in the form of sulphates, but is in an organic form, and it is not surprising that it is lost under the conditions. The same would be true of *chlorine*, which is probably much more difficult to retain than sulphur.

The following modification of the nitric acid method just described has been found more convenient. It calls for the use of a smaller quantity of material, and leaves out the platinum dish, which is liable to be damaged under certain conditions.

Five grams material are placed in a 3½ inch porcelain evaporating dish, 20 cc. of concentrated nitric acid added, and the mixture heated cautiously on the water-bath until all danger of overflowing has passed. It is then partly evaporated, 10 cc. of a

5 per cent. solution of potassium nitrate added, the mixture evaporated to dryness and ignited, at first gently, then under a blast-lamp, until the residue is white. It is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air-bath to render silica insoluble. The residue is taken up in water with the addition of a little acid, filtered, and the sulphuric acid precipitated with barium chloride, etc., in the usual way.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 61].

ON THE RELATION OF THE HEAT OF COMBUSTION TO THE SPECIFIC GRAVITY IN FATTY OILS.

BY H. C. SHERMAN AND J. F. SNELL.

Received January 4, 1902.

FROM data given in a previous paper[1] it was inferred that among the common fatty oils there exists a certain definite relation between the heat of combustion and the specific gravity. Thus, comparing such typical oils as those of linseed, poppyseed, maize, cottonseed, sesame, almond, and olive, we find that the decrease in drying properties is accompanied by a decrease in specific gravity and a nearly proportional increase in the calorific power, so that the product of these two values shows comparatively little variation. It also seemed probable from the examination of a few samples which were known to have been oxidized by exposure, that such oxidation reduces the heat of combustion to nearly the same extent that it increases the specific gravity. We are now able to give additional data in support of each of these inferences.

The determinations of specific gravity and of heat of combustion have been made by the methods described in our previous paper and we are again indebted to Professor Atwater, for the privilege of doing a considerable part of the work in the laboratories of Wesleyan University. The heats of combustion given in the tables below are those obtained at constant volume; *i. e.*, the results actually shown by the calorimeter. The corresponding values for combustion at constant pressure may be calculated as already explained.[2]

Table A shows the specific gravities and heats of combustion

[1] This Journal, **23**, 164.

[2] *Ibid*, **23**, 167.

of the fatty oils thus far examined which were either fresh or had been well protected from the air, so that no considerable oxidation is believed to have taken place. The last two columns give respectively the product obtained by multiplying, and the quotient obtained by dividing the heat of combustion (in large calories per gram) by the specific gravity. A few non-fatty oils are added at the end of the table.

TABLE A.—RELATION OF SPECIFIC GRAVITY TO HEAT OF COMBUSTION IN FATTY OILS WHEN FRESH.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5°}{15.5°}$.	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2052	Raw linseed, I	0.934	9.364	8.74	10.03
2070	Raw linseed, II	0.938	9.379	8.80	10.00
2122	Raw linseed, IV	0.933	9.381	8.75	10.05
Aver.	Raw linseeds	0.935	9.375	8.77	10.03
2073	Boiled linseed, I	0.934	9.394	8.77	10.06
2127	Boiled linseed, II	0.935	9.349	8.74	10.00
Aver.	Boiled linseeds[1]	0.935	9.372	8.76	10.02
2069	Poppyseed	0.926	9.382	8.69	10.13
2056	Maize oil, I	0.924	9.413	8.71	10.19
2066	Maize oil, II	0.926	9.436	8.74	10.19
2092	Maize oil, III (dark)	0.926	9.419	8.72	10.17
Aver.	Maize oils	0.925	9.423	8.72	10.19
2063	Sesame	0.924	9.395	8.68	10.17
2053	Cottonseed, I	0.920	9.396	8.64	10.21
2054	Cottonseed, II	0.921	9.401	8.66	10.21
2055	Cottonseed, III	0.923	9.390	8.67	10.17
2089	Cottonseed, IV (dark)	0.927	9.397	8.71	10.14
Aver.	Cottonseed oils	0.923	9.396	8.67	10.18
2102	Rape, I	0.920	9.489	8.73	10.31
2065	Rape, II	0.920	9.462	8.71	10.29
Aver.	Rape oils	0.920	9.476	8.72	10.30
2061	Peanut (arachis)	0.917	9.412	8.63	10.26
2064	Almond	0.919	9.454	8.69	10.29
2058	Olive, I	0.917	9.457	8.67	10.31
2093	Olive, II	0.916	9.451	8.66	10.32
Aver.	Olive oils	0.917	9.454	8.67	10.31
2091	Castor	0.967	8.863	8.57	9.17
2062	Castor	0.964	8.835	8.52	9.16
Aver.	Castor oils	0.966	8.849	8.55	9.16
2076	Menhaden	0.935	9.360	8.75	10.01

[1] Only boiled linseed oils of low specific gravity are here included. Data of other samples are given in Table B. It was recently found that the figures given for boiled linseed oil in our previous paper were incorrect. Through an error the heat of combustion was determined on a sample different from that in which determinations of specific gravity, iodine absorption, and acidity had been made.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5°}{15.5°}$	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2077	Menhaden	0.934	9.371	8.76	10.03
Aver.	Menhaden oils	0.935	9.366	8.76	10.02
2104	Cod-liver	0.926	9.434	8.74	10.19
1998	Cod-liver	0.927	9.437	8.75	10.18
Aver.	Cod-liver oils	0.927	9.436	8.75	10.18
2103	Seal oil	0.926	9.424	8.73	10.18
2084	Whale oil	0.924	9.473	8.75	10.25
2057	Lard oil, I	0.917	9.451	8.67	10.31
2060	Lard oil, II	0.919	9.447	8.68	10.28
Aver.	Lard oils	0.918	9.449	8.67	10.29
2080	Sperm oil	0.886	9.946	8.81	11.23
2081	Rosin oil	0.989	10.145	10.03	10.26
2098	Petroleum oil, I	0.881	10.797	9.51	12.26
2099	Petroleum oil, II	0.897	10.753	9.64	11.99
2100	Petroleum oil, III	0.905	10.682	9.67	11.80
Aver.	Petroleum oils	0.894	10.744	9.61	12.01
2143	Turpentine	0.862	10.800	9.31	12.52

Excepting the castor oils, which, of course, differ from all the others in containing a large proportion of ricinolein, the value obtained by multiplying the heat of combustion by the specific gravity shows very little variation as between oils of the same variety, while as between the different classes of oils this value decreases with the specific gravity, but to a less degree. The value obtained by dividing the heat of combustion by the specific gravity varies, of course, in the opposite direction and to a greater degree. Thus the difference between these two values increases as we pass from the oils of higher to those of lower specific gravity. These relations hold as well for the fatty oils of animal as for those of vegetable origin. The non-fatty oils, on the other hand, show quite different relations.

Table B shows the results obtained upon a number of commercial oils which had specific gravities higher than the corresponding fresh oils and which are believed to have been more or less oxidized by exposure to the air. In nearly all cases such exposure is known to have occurred. A sample of blown rapeseed oil is also included.

TABLE B.—RELATION OF SPECIFIC GRAVITY TO HEAT OF COMBUSTION IN "EXPOSED" FATTY OILS.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5°}{15.5°}$	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2082	Raw linseed, III	0.947	9.215	8.73	9.73
2123	Raw linseed, V.....	0.941	9.274	8.73	9.86
2124	Raw linseed, VI	0.952	9.099	8.66	9.56
Aver.	Raw linseeds	0.947	9.196	8.71	...
2072	Boiled linseed, III.....	0.949	9.191	8.72	9.69
2125	Boiled linseed, IV.....	0.951	9.152	8.70	9.62
2126	Boiled linseed, V.....	0.944	9.275	8.76	9.83
Aver.	Boiled linseeds.....	0.948	9.206	8.73	...
1999	Cottonseed, V (dark)	0.927	9.336	8.65	10.07
2087	Cottonseed, VI.....	0.929	9.323	8.66	10.04
2067	Cottonseed, VII (old).....	0.941	9.168	8.63	9.74
Aver.	Cottonseed oils	0.932	9.276	8.65	...
2086	Rapeseed.....	0.926	9.412	8.72	10.16
2111	Blown rapeseed	0.974	8.805	8.58	9.04
2094	Almond	0.931	9.311	8.67	10.00
2085	Cod-liver	0.938	9.277	8.70	9.89
2059	Lard oil, III	0.924	9.372	8.66	10.14
2095	Lard oil, IV	0.922	9.394	8.66	10.19
Aver.	Lard oils	0.923	9.383	8.66	....

In this table the figures in the last column are, of course, lower than the corresponding figures in Table A and are quite variable, being dependent upon the extent to which the samples had become oxidized. The values obtained by multiplying the heat of combustion by the specific gravity are very little different from the corresponding values in Table A; in other words, the effect of exposure was to cause an increase in specific gravity and a nearly equal decrease in heat of combustion.

In general the oils which had been exposed showed slightly more free acid than those in Table A. Hydrolysis of fat with liberation of fatty acid involves an absorption of water. To split off 1 per cent. of oleic acid, about 0.06 per cent. of moisture must be taken up. The oils examined contained very little free acid and for our purpose it is probably safe to neglect the small amounts of water involved. It may be noted, however, that any moisture thus taken up would lower the heat of combustion more than it would raise the specific gravity, thus decreasing the value of the product of these two factors; and it will be seen that such slight discrepancies as are found by a comparison of Tables A and B are always in this direction.

Sample No. 2067, an old cottonseed oil, shows such remarkable results that (as the history of the sample was not known) it seemed advisable to determine the elementary composition, in order to confirm the assumption that its peculiar properties were due to oxidation. It yielded, on analysis,

	Per cent.
Carbon	73.66
Hydrogen	11.34
Oxygen	15.00

Sample No. 2054, which was known to be fresh and was selected as being typical, yielded

	Per cent.
Carbon	76.65
Hydrogen	11.74
Oxygen	11.61

The increased percentage of oxygen found in the older sample is quite sufficient to account for the observed differences in specific gravity and heat of combustion; and while the elementary analyses are not in exact proportion to these differences, the agreement is perhaps as close as could be expected between samples produced by different methods at an interval of several years.[1]

Conclusions drawn from a comparison of the figures given in Table B, with those in Table A are open to objection inasmuch as the samples of "fresh" and of "exposed" oils of a given variety are not always from the same source, though the fact that the relations noted apply to each of the seven varieties included in the comparison makes it improbable that they are accidental.

In raw and boiled linseed oils, however, we have obtained sufficient oxidation by exposure in uncorked bottles for two to four months, to give positive confirmation of the inferences already drawn. Thus sample No. 2052, raw linseed oil, and sample No. 2072, boiled linseed oil, gave the following :

[1] A similar comparison was attempted in the case of the blown rape oil (No. 2111), No. 2102 being selected as a typical fresh sample for comparison. The latter yielded : Carbon, 76.23 per cent.; hydrogen, 11.52 per cent.; oxygen, 12.25 per cent. The blown oil yielded figures for carbon ranging from 71.22 to 73.00 per cent., and for hydrogen from 10.61 to 11.09 per cent. This would indicate that the extremely high viscosity of the sample prevented thorough mixing, in which case the determination of heat of combustion may also be less accurate than in the other samples. In general terms, however, it may be said that the increased percentage of oxygen in the blown oil corresponds approximately to the increase in specific gravity and decrease in heat of combustion.

	Sp. gr. at 15.5°.	Calories per gram.	Calories × sp. gr.
Raw linseed before exposure	0.934	9.364	8.74
Same after four months' exposure ...	0.942	9.288	8.75
Boiled linseed before exposure.....	0.949	9.191	8.72
Same after two months' exposure....	0.9595	9.078	8.71
Same after four months' exposure ...	0.968	8.963	8.68

The boiled linseed oil after four months' exposure was so thick that the determinations made upon it may be less accurate than in the other cases. Elementary analyses were made of the boiled linseed oil, before and after the two months' exposure, with the following results:

	Carbon.	Hydrogen.	Oxygen.
Before exposure	75.02	10.73	14.25
After exposure.....	74.15	10.70	15.15

Here the exposure, while raising the specific gravity 1.1 per cent. and lowering the heat of combustion 1.2 per cent., has lowered the combined percentages of carbon and hydrogen 1.1 per cent. of the amount originally present.

The simplest interpretation of these relations would be that the oil took up from the air an amount of oxygen equal to 1.1 per cent. of its original weight and that this oxygen was absorbed without appreciable increase of volume or loss of carbon or hydrogen. It seems probable also that each of the oils shown in Table B above had absorbed oxygen in the same manner.

A study of the quantitative relations of the changes produced by such oxidation in the usually determined "constants" is being carried on in this laboratory, and it is hoped that this may lead to more definite knowledge of the significance of these constants.

We believe that the data here given justify the following conclusions:

1. In fresh fatty oils the heat of combustion is a property quite as constant as the specific gravity, to which it bears a certain definite relation.

2. Oxidation resulting from exposure to air decreases the heat of combustion to practically the same extent that it increases the specific gravity. Hence it is to be inferred that the oxygen is taken up by direct addition and without essential change in the volume of the oil.

3. On account of its close quantitative relations to the specific gravity and ultimate composition, the heat of combustion is likely to prove a useful factor in the further study of the fatty oils.

NEW YORK CITY, January 2, 1902.

ACTION OF SELENIC ACID ON GOLD.[1]

By Victor Lenher.

Received January 6, 1902.

In a number of text-books and works of reference on chemistry, it is stated that gold is attacked by hot selenic acid, the latter being reduced. The details of the reaction do not seem to have been worked out, nor the products investigated.

The statement that gold is dissolved by selenic acid finds its origin in the work of Mitscherlich,[2] who was the first to prepare and study the properties of selenic acid. He states that selenic acid dissolves gold but not platinum.

Inasmuch as selenic acid in presence of hydrochloric or hydrobromic acid is reduced to selenious acid with the liberation of halogen, which would act on gold, and since no selenate of gold appears to be described in the literature, it seemed well to investigate this reaction and ascertain whether gold would dissolve in pure selenic acid which contained no halogen, and if solution actually took place, what the products of the reaction would be.

In order to preclude the possibility of the presence of a halogen in the selenic acid used, the acid was prepared as follows: Resublimed selenium dioxide was fused with pure potassium nitrate. The resulting selenate was dissolved in water and to a dilute solution, a solution of lead nitrate was added; the resulting precipitate of lead selenate was repeatedly washed with water until pure. It was then suspended in water and treated with hydrogen sulphide gas. Lead sulphide was obtained along with any selenium existing as selenite. The dilute selenic acid which resulted was concentrated on the water-bath and was used in the following work. For a preparation of a part of the selenic acid used, the author is indebted to Mr. W. H. Richardson.

The fairly concentrated acid which was thus obtained was brought into contact with gold leaf. No action was apparent in the cold. By evaporation, it is possible to concentrate selenic acid, and when the acid is hot and concentrated, gold dissolves readily to a reddish yellow solution. The action begins at about 230°, but proceeds much more readily at about 300°; selenium dioxide is evolved, while the gold goes into solution as auric sele-

[1] Read at the Philadelphia meeting of the American Chemical Society.

[2] Pogg. *Ann.*, **12**, 630.

nate, $Au_2(SeO_4)_3$. Analysis of the salt showed that it agrees with this formula. The gold leaf was replaced by small pieces of gold, and it was found that the latter dissolve nearly as readily as the leaf and at about the same temperature. In most respects the action is similar to that of sulphuric acid on copper, although no such complicated products arise as mentioned by Baskerville[1] in the study of this reaction.

The selenate has been obtained as very small yellow crystals. It is soluble in hot concentrated selenic acid, forming a reddish-yellow solution, and separates on cooling. It is insoluble in water, and can be completely separated from selenic acid by dilution, when it appears as a yellow precipitate. It is soluble in sulphuric acid and in nitric acid. Hydrochloric acid decomposes the salt with evolution of chlorine, forming auric chloride and selenious acid. It is decomposed by heat below redness, metallic gold being obtained. On exposure to the light, auric selenate is decomposed, becoming dark green then bronze colored. It is worthy of note that all the members of the subgroup B in the first group of the periodic system, dissolve in selenic acid with evolution of selenium dioxide and formation of the corresponding selenate. Silver dissolves in selenic acid when the latter is hot and concentrated, the selenate being produced and selenium dioxide being evolved. Copper also acts in a similar manner. During the solution of gold in selenic acid, selenium dioxide is produced, being evolved as fumes, and is also invariably found in the solution after the reaction. Moreover in the reaction of selenic acid on gold we have for the first time the solution of gold in a simple oxygen acid.

UNIVERSITY OF WISCONSIN,
MADISON, WIS.

NATURALLY OCCURRING TELLURIDE OF GOLD.[2]

BY VICTOR LENHER.

Received January 6, 1902.

THE occurrence of gold in nature, according to the commonly accepted view, is either as native gold or as telluride. It is generally conceded that gold exists in pyrite or other sulphide ores uncombined and in the elementary condition. This, broadly speaking, is the manner in which gold is considered to exist in nature. No mineral containing gold as one of its constituents,

[1] Baskerville: This Journal, **17**, 904.

[2] Read at the Philadelphia meeting of the American Chemical Society.

and no chemical compound of gold is known in nature with the possible exception of the so-called "tellurides" or the tellurides of gold.

It is the purpose of this paper to describe a series of experiments which have been conducted with the view of throwing some light on the constitution of the naturally occurring tellurides.

The peculiar combinations of gold and tellurium which occur in nature have a more or less definite and more or less indefinite character, both from the standpoint of the chemical mineralogist and of the crystallographer. The recorded analyses of the telluride minerals show considerable variation from a constant composition.

One of the best defined compounds of gold and tellurium occurring in nature, and the compound which contains the nearest to pure tellurium and gold has been called "calaverite."

Calaverite is a silver-white mineral, frequently possessing striated faces, containing in composition from 55.8 to 57.6 per cent. tellurium, 40.6 to 42.7 per cent. gold, and smaller quantities of silver, 0.40 to 3.0 per cent. The theoretical requirements for $AuTe_2$ are 56.32 per cent. tellurium and 43.68 per cent. gold. This mineral contains more gold and less silver than the other tellurides. This combination of gold and tellurium appears to present some definite characteristics of a mineral. The recent work of Penfield and Ford[1] seems to throw some doubt on the definiteness of its crystallographic constants. In this valuable paper, measurements of crystal faces are given, which show either monoclinic or triclinic symmetry.

Sylvanite, one of the most common tellurides of Colorado and West Australia, occurs in brilliant white twinned crystals which are frequently distributed over the faces of rocks in such a manner as to resemble Arabic writings; hence, it has been called "graphic tellurium." This mineral contains about 60 per cent. tellurium, 16 per cent. gold, and 14 per cent. silver. Other tellurides, which are well defined, are krennerite and petzite.

Finally, from the recorded analyses of native tellurium, gold is not infrequently found to be present.

In the investigation of the tellurides, the author has been extremely fortunate in having had placed at his disposal the fine collection of tellurides of the University of Wisconsin, through

[1] *Am. J. Sci.*, p. 225, September, 1901.

the courtesy of Professor W. H. Hobbs, of the department of mineralogy.

In some investigations now being carried out by Hall and Lenher, on the action of metallic tellurium on gold and silver salts, it has been observed that tellurium quantitatively precipitates gold from solution in the ratio of 4Au : 3Te, according to the equation

$$4AuCl_3 + 3Te = 4Au + 3TeCl_4.$$

When a solution of chloride of gold is added to metallic tellurium, metallic gold is deposited, tellurium tetrachloride passing into solution. The reaction is accelerated by heating the solution, and time is a considerable factor as far as quantitative results are concerned. If proper precautions are observed and the gold salt is in excess, the above ratio will be obeyed.

Likewise, when tellurium is introduced into a silver solution, similar results are obtained. The reaction, as thus far studied, appears not to be as sharp as with gold, nor as complete; nevertheless, our results have demonstrated that from a silver solution, no matter whether an aqueous solution of fused silver nitrate, ammoniacal silver nitrate, or ammoniacal silver chloride be used, metallic silver is obtained.

The action of elementary selenium on gold solutions has also been studied, and the results obtained show that selenium acts as a reducing agent to gold salts, throwing the metal out of solution.

When these facts had been ascertained, the natural tellurides were tested to determine their behavior to chloride of gold. Sixteen specimens of the minerals from different sources were tested, and in each case, when the telluride mineral was brought into contact with a chloride of gold solution, metallic gold was obtained. The minerals examined were:

One specimen calaverite, Abe Lincoln Mine, Cripple Creek, Colorado.

One specimen calaverite, Little May Mine, Cripple Creek, Colorado.

One specimen calaverite, Porcupine Mine, Cripple Creek, Colo.

Five specimens calaverite, Gold Coin Mine, Victor, Colorado.

One specimen sylvanite, Battle Creek Monument, Cripple Creek, Colorado.

Two specimens sylvanite, Magnolia, Boulder County, Colorado.

One specimen sylvanite, Offenbanya, Hungary.

One specimen coloradoite, West Australia.

Two specimens kalgoorlite, West Australia.

One specimen nagyagite, Nagyag, Austria.

All of these minerals precipitated metallic gold from the solution of chloride, and when only a small quantity of gold solution was used, the latter was bleached from yellow to completely colorless.

The question naturally arises at this point, whether a chemical compound can precipitate one of its constituents in such a manner as shown in this reaction. An attempt was then made to prepare telluride of gold artificially with a view of studying its composition and properties.

In the elaborate research of Brauner[1] on the atomic weight of tellurium, an attempt was made to synthesize telluride of gold. He obtained "crystalline polytellurides (alloys of gold and tellurium) of a silvery lustre," but not definite in composition. Au_2Te is the nearest approximation to a definite formula. Brauner's work has been repeated by me. Gold mixed with an excess of tellurium was placed in a porcelain boat and heated to redness in a current of carbonic acid. Under these conditions, tellurium distils on heating, and the amount given off is entirely dependent on the temperature and length of heating. After conducting this experiment for six hours, the material remaining in the boat had a golden appearance. On removing this substance, which appeared in globules, from the boat, it was found to consist of an outer shell or crust of gold, covering a white alloy-like substance. Inasmuch as this white body, on being brought in contact with chloride of gold solution, precipitates metallic gold, it is hardly likely that it is a definite chemical compound.

Another series of experiments was conducted with a view of preparing telluride of gold in the wet way. Hydrogen telluride generated by the action of dilute hydrochloric acid on aluminum telluride, was conducted into a solution of chloride of gold; a golden colored precipitate was formed. This precipitate was collected and carefully analyzed, and was found to be pure gold. The experiment was repeated, precipitating first only a part of the gold, then adding an excess of hydrogen telluride and precipitating completely. These fractions were separately analyzed, and in all cases the precipitates formed by the action of hydrogen telluride on gold solutions were found, by actual weight, to be

[1] *J. Chem. Soc.*, **55**, 391.

pure gold, and in no precipitate could even a trace of tellurium be detected. According to these results, hydrogen telluride does not form telluride of gold, or at all events, telluride of gold has not appeared thus far in the wet way. All attempts which have been made thus far for the preparation of artificial telluride of gold have been unsuccessful.

At this point, it might be well to add that an attempt to precipitate gold and tellurium together has been unsuccessful. To a solution containing 0.1089 gram gold and 0.1404 gram tellurium as chlorides, sulphur dioxide was added, with the hope that possibly the compound $AuTe_2$ might be precipitated. The result was first a precipitation of gold followed by tellurium. Had any tellurium come down at first, on coming in contact with the gold in solution, it would have precipitated the latter. The entire precipitate was collected, dried, and fused in carbon dioxide. It gave a white alloy which precipitated gold from a solution of gold chloride.

Recent work[1] on the action of sulphur monochloride on metallic tellurium has shown that when these two substances come in contact, tellurium tetrachloride is formed, and being insoluble in chloride of sulphur, separates in white needle-like crystals. The action is represented by the equation

$$Te + 2S_2Cl_2 = TeCl_4 + 4S.$$

The free sulphur formed as indicated in the reaction goes into solution in the excess of sulphur chloride.

The entire series of naturally occurring tellurides when subjected to the action of sulphur monochloride lost their tellurium, leaving gold as a residue, and in a number of cases the tellurium immediately separated as crystals of tetrachloride.

Another reaction of these minerals, which perhaps has not as much significance from the chemical standpoint, is that with nitric acid. When the minerals are treated with nitric acid, the tellurium and silver dissolve, leaving the gold as a residue.

SUMMARY.

1. Metallic tellurium quantitatively precipitates gold from solution. A similar reaction takes place with silver, though possibly not so completely. Selenium acts as a reducing agent with solutions of these metals, but is not as strong a reducing agent as tellurium.

[1] This Journal, **24**, 188.

The tellurides of nature act towards gold solutions unlike a chemical compound of gold and tellurium, in that they throw gold out of solution.

It is not infrequent to find specimens of native gold in the same mine with the tellurides. The author has observed yellow or golden incrustations as a superficial coating on natural crystals of calaverite and sylvanite, while immediately under this coating the silver-white telluride was found; when this white material was brought into contact with gold chloride, metal was obtained.

Professor C. R. Van Hise informs the author that he has seen many beautiful specimens of gold from Cripple Creek which are pseudomorphs after the tellurides, showing both the crystalline form and striations of the original mineral.

2. Thus far the attempts to prepare telluride of gold artificially either in the wet way or the dry way have been unsuccessful.

3. It is possible to extract the tellurium from these minerals, leaving the noble metal as a residue.

CONCLUSIONS.

In view of the facts above ascertained, much doubt seems to be cast as to whether the tellurides are definite chemical compounds. The fact that they all precipitate metallic gold from solution, and lose their tellurium with such reagents as sulphur chloride, are points which are difficult to reconcile with a chemical compound.

The observation that hydrogen telluride in contact with gold solutions instead of forming telluride of gold, acts as a reducing agent, throwing out pure gold, may also be regarded as significant, and as well the fact that the body of inconstant composition containing tellurium and gold, obtained at high temperatures, reduces gold chloride, appears to place the telluride minerals in a very doubtful light as chemical compounds.

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SOME COMPOUNDS OF PYRIDINE.

BY J. ARTHUR HAYES.

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WHEN some compounds of the metals with the halogens, in solution of that halogen acid, are brought in contact with the halogen acid compound of pyridine, addition-products

are formed of a crystalline structure, the composition varying with the method of preparation.

In view of this fact the author has been able to prepare several compounds of pyridine, the following of which have not been described :

THE COMPOUND $C_5H_5N.SbBr_3.3HBr$.

Pyridine hydrobromide is prepared by adding hydrobromic acid to pyridine, an excess of acid being used to prevent crystallization. As considerable heat is evolved, the vessel containing the hydrobromide is cooled under the tap, and then a solution of antimony bromide in hydrobromic acid is added with caution.

Upon the addition of the acid solution of antimony bromide to the pyridine hydrobromide, there is more evolution of heat and the formation of a yellow crystalline precipitate. This is allowed to stand for a time to insure complete precipitation and then filtered off by means of a suction-pump. For purification the salt is stirred in a vessel with ethyl alcohol (95 per cent.), and again filtered and washed with alcohol until the filtrate contains no traces of free pyridine, antimony or hydrobromic acid.

The antimony was determined as the sulphide and the bromide by titration with decinormal silver nitrate with potassium chromate as an indicator. Pyridine and the hydrogen of the compound were obtained by difference.

An average of several analyses gave :

	Calculated for $C_5H_5N.SbBr_3.3HBr$.	Found.
Antimony	17.6	18.5
Bromine	70.3	70.4
Pyridine and hydrogen	12.1	11.1

Properties.—$C_5H_5.N.SbBr_3.3HBr$ is in the form of small yellow crystals. It is soluble in dilute hydrochloric acid, insoluble in ether and benzene; very slightly soluble in ethyl alcohol and chloroform.

When treated with nitric acid the oxide of antimony is formed; when treated with water a basic hydroxide of antimony is formed, and heating the salt dry decomposes it to the oxide of antimony.

THE COMPOUND $C_5H_5N.SnCl_2.3HCl$.

Preparation.—The process is the same as for the preparation of the antimony salt with the exception of hydrochloric acid, in-

stead of hydrobromic being used as a solvent for the metallic salt and to form the acid halogen salt of pyridine.

The analysis gave:

	Calculated for $C_5H_5N.SnCl_2.3HCl$.	Found.
Tin	28.07	28.5
Chlorine	50.20	50.75
Pyridine and hydrogen	21.73	20.75

Properties. — $C_5H_5N.SnCl_2.3HCl$ crystallizes in small white needle-shaped crystals. It is decomposed by water into a basic hydroxide or oxide of tin, and by nitric acid into the oxide of tin. When heated, the oxide of tin is the decomposition product. It is soluble in dilute hydrochloric acid, insoluble in ether, benzene, and chloroform, and very slightly soluble in 95 per cent. alcohol.

THE COMPOUND $C_5H_5N.MnCl_2.HCl$.

Preparation.—The process is the same as for the preparation of the tin salt. A great deal of care has to be taken in the purification by 95 per cent. alcohol as the compound is quite soluble. The manganese was determined by precipitation with sodium carbonate and was weighed as Mn_3O_4.

The analysis gave:

	Calculated for $C_5H_5N.MnCl_2.HCl$.	Found.
Manganese	22.70	21.57
Chlorine	44.00	44.10
Pyridine and hydrogen	33.30	34.33

Properties.—$C_5H_5N.MnCl_2.HCl$ crystallizes in salmon-colored plates. It is soluble in 95 per cent. alcohol and hydrochloric acid, slightly soluble in ether and insoluble in chloroform. When heated, decomposition takes place with the formation of the oxide of manganese.

UNIVERSITY OF MAINE CHEMICAL LABORATORY,
June, 1901.

COMMON ERRORS IN THE DETERMINATION OF SILICA.[1]

BY W. F. HILLEBRAND.

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TO some it may seem as if a threadbare subject had been reopened in the above title, and that concerning a determination of such common occurrence in both technical and scientific

[1] Read at the Philadelphia meeting of the American Chemical Society.

operations little remained to be said or done. But that this is not so the following presentation will, I think, make sufficiently clear. Although not much of what I shall offer is really new, even that which is not will well bear repetition, having escaped the attention which it deserves. It seems to be advisable and necessary that public attention should be from time to time called to important facts which have not impressed themselves sufficiently to become a matter of common knowledge and application.

Regarding certain features of the silica determination I have long entertained doubts, but it is only very recently that convenient opportunity has presented itself for an investigation of these points as well as others, the direct incentive being afforded by an experience of the past summer as an outgrowth of the labors of a Committee of the New York Section of the Society of Chemical Industry having for its object the promotion of uniformity in technical analysis.

Uniform samples of raw cement-mixture and of finished cement were sent to a large number of analysts for determination of the commoner constituents by the usual technical methods. The same samples were analyzed in greater detail by myself and with the same regard to exactness that is usual in analyzing rocks and minerals in the laboratory of the United States Geological Survey. Fourteen of the chemists besides myself returned reports which showed in most cases a marked lack of agreement. The results for silica[1] only are here presented in tabular form with one exception, which is omitted for the reason that it does not profess to represent silica only, but rather the residue from evaporation of the limestone with acid, hence containing much undecomposed mineral matter.

TABLE I. SILICA FOUND BY DIFFERENT ANALYSTS IN THE SAME SAMPLES OF RAW MIXTURE AND FINISHED CEMENT.

	Limestone mixture.	Finished cement.
Standard	15.18	21.31
1	15.75	20.90
1*a*	15.37	——
2	14.68	20.92

[1] The full data together with copies of the outlines of methods employed were submitted to me for review and suggestion without knowledge on my part of the names of the analysts. My report was transmitted through the Director of the Geological Survey to the committee of the New York Section of the Society of Chemical Industry, and its report was rendered at the Section meeting on December 20, 1901, and published in the *J. Soc. Chem. Ind.*, Jan. 15, 1902.

	Limestone mixture.	Finished cement.
3	13.92	20.06
4	——	20.00
5	14.18	20.26
6	14.70	20.96
7	12.78	20.84
8	13.97	19.82
9	14.44	20.76
10	13.60	19.18
11	14.64	21.46
12	14.18	20.76
13	14.92	21.56
14	13.56	19.53
Highest	15.75	21.56
Lowest	12.78	19.18
Difference	2.87	2.38

Without detailing the various means employed for rendering silica insoluble it may be said that all the workers strove to bring this about by the usual more or less approved methods of drying at temperatures ranging from that of the steam-bath for a long time to 120° and even higher for a shorter time. Despite their efforts there is not only a wide discordance in results, but, with two exceptions in each series, they are all too low. The actual failure to recover all silica is, however, in the majority of cases greater than the figures indicate, by reason of neglect of blast-ignition, or of correction by hydrofluoric acid, or both.

It is evident then that none of the methods in common use for rendering silica insoluble can be at all depended on to effect this result. None of the analysts except No. 1 and myself seems to have employed two evaporations with an intervening filtration. All others made but a single filtration, and in this simple difference lies the main solution of the trouble, a fact pointed out by Alex. Cameron with quantitative demonstrations nearly eight years ago,[1] but which has apparently almost escaped the notice of chemists. Indeed I must admit a certain degree of remissness myself, for I have but an indistinct recollection that it was the reading of Cameron's paper when it first appeared which led me to adopt the practice of double evaporations with intervening filtrations which I have followed for a good many years. What influenced this change had escaped my mind until mention of

[1] *Chem. News*, **69**, 171 (1894).

Cameron's paper in a recent number of this Journal, followed by its reperusal, recalled the matter to recollection.

Other earlier writers, as Lindo, Craig, and Gilbert, have recognized the impossibility of recovering all silica by one evaporation, without, however, recommending a repetition after filtration. Instead, dehydration by hot sulphuric acid is often used in iron and steel works, but its use precludes satisfactory determination of other constituents in the same sample.

Cameron used in most of his experiments 2 grams of silica, about 98½ per cent. pure, fused this with 9 grams of fusion mixture, dissolved the fused mass in hydrochloric acid, and evaporated in porcelain on the water-bath. The drying was continued on the bath in several experiments for some time after all acid fumes had ceased; in others the dehydration was effected by the blue flame of an Argand burner. He found that with the lower temperature four, and even five, evaporations and filtrations were needed to reduce the silica recovered to a negligible quantity, but that with the higher heat three, or even sometimes two, sufficed. Furthermore, he showed by one experiment that a very common practice of evaporating several times to dryness with fresh portions of acid without intervening filtrations did not reduce the silica in the filtrate, and that the presence of aluminum, iron and calcium was without influence on the results.

My own experiments to test all these points were entirely confirmatory of Cameron's, though less unfavorable as to the number of evaporations needed. This I attribute to the facts that I employed from one-half to one-fourth as much silica as he did, thus conforming more nearly to the ordinary conditions of a silicate analysis, and platinum instead of porcelain evaporating dishes. On the water- or steam-bath drying is not so speedily reached in porcelain as in platinum, and very possibly his later siliceous residues came in large part from the vessel itself.

The material employed in my tests was very nearly pure quartz crystal containing 99.88 per cent. silica. Amounts of this lying usually within the limits 0.5 and 1 gram were fused with 5 grams sodium carbonate, the fused masses dissolved in hot water, then acidified by hydrochloric acid, and the solutions evaporated in platinum vessels for different lengths of time on a steam-bath. Then the residues were digested for a short time with hydrochloric acid and hot water. Prolonged digestion was unnecessary, as

only sodium chloride with mere traces of other salts had to be extracted.

TABLE II. SILICA FOUND IN FILTRATES.

	Weight of quartz	SiO_2 in first filtrate.	Per cent.	SiO_2 in second filtrate.	
1..	0.8943	0.0078	= 0.87	0.0012	Duration of first drying not known.
2..	0.8208	0.0321	= 3.91	0.0006	Duration of first drying brief, not exceeding one to two hours, and in one case the residue still somewhat moist in parts.
3..	0.6401	0.0218	= 3.41	0.0005	
4..	0.5738	0.0197	= 3.43	0.0009	
5..	0.7028			0.6000	
6..	0.5931	0.0167	= 2.82	0.0001	Duration of first and second dryings twenty-one hours each. In 9 the mass was ground to powder as soon as free from visible moisture, without marked improvement in the result.
7..	0.7309	0.0211	= 2.89	0.0001	
8..	0.8495	0.0204	= 2.40	0	
9..	0.7841	0.0142	= 1.81	?	
10..	0.7092	0.0089	= 1.25	0.0004	Several evaporations with fresh acid before first filtration. Total duration of dryings and evaporations twenty hours.
11..	0.7324	0.0047	= 0.64	0.0005	Repeated (4) evaporations with water only before first filtration, twenty hours' drying before third filtration.
12..	2.0000	0.0193	= 0.96	0.0008	

Experiment 10 was made in order to test the somewhat prevalent practice of evaporating several times with fresh acid before filtering. The result is an improvement over all but the first of the earlier ones, but still leaves much to be desired.

Experiments 11 and 12, in which repeated evaporations with water only were made, show a still better but by no means satisfactory result. The improvement in these last cases is not surprising, but it is to be expected that in ordinary analysis the foreign matter remaining with the silica would be increased by this treatment with water only instead of acid.

In order to learn, if possible, something about the effect of the large amount of sodium chloride in preventing the dehydration of silica, a soluble gelatinizing zeolite (thomsonite with 41.17 per cent. silica) was experimented with. The foreign chlorides in solution were here, of course, very much reduced in amount. The results are shown opposite 1, 2, 3 of table III.

TABLE III. SHOWING DIFFERENT SOLUBILITIES OF THE SILICA SEPARATED IN GELATINOUS AND GRANULAR FORM FROM ZEOLITES.

	SiO_2 in weight of zeolite taken.	SiO_2 in first filtrate.	Per cent.	
1.....	0.4185	0.0065	1.55	Duration of drying 2 hours.
2.....	0.4142	0.0048	1.16	Duration of drying 21 hours.
3.....	0.8265	0.0072	0.87	Duration of drying 21 hours.
4.....	0.5736	0.0020	0.35	Duration of drying brief.
5.....	0.5760	0.0023	0.40	Duration of drying prolonged.

Since the separation of silica from soluble silicates occurs in two forms, gelatinous and granular, according to the species acted on, it seemed worth while to try a non-gelatinizing zeolite (heulandite) containing 57.18 per cent. silica. The results appear opposite Nos. 4 and 5 of Table III. Manifestly the instantaneous separation of silica in granular form, without first entering into solution, is far more perfect than when it gelatinizes.

We have thus seen how the serious errors in silica determinations shown by Table I can be avoided by two evaporations with intervening filtrations. In extreme cases a third evaporation may at times be advisable. Furthermore, that prolonged drying is a useless waste of time, except perhaps after the second evaporation, when, if results like 6, 7, and 8 of Table II can be depended on, it may be of value in very exact work.

CAUSES OF THE SOLUBILITY OF SILICA UNDER THE CONDITIONS GIVEN.

In explaining the partial solubility of silica after drying at temperatures much above that of the water-bath it has been customary to assume the formation of soluble silicates by action between some of the silica and salts present. This is an undoubted cause and one which should become more active with increasing temperature, though Gilbert's work does not seem to indicate this except when magnesium is present in quantity. But if true at 120° it must probably still be true to some extent at 100°.

Another explanation for the incomplete dehydration at 100° is assumed to be the protecting influence of other salts, and to remedy this, repeated additions of acid, or perhaps better still of water, are sometimes resorted to (See Exp. 10–12 of Table II).

Again it may be that the silica separated is itself soluble enough in acid to cause an appreciable error. The experiments reported below show clearly what the action of hydrochloric acid is on silica which had been obtained by fusing quartz with sodium carbonate and drying the evaporated hydrochloric solution for twen-

ty-one hours on the steam-bath. This silica (about 0.65 gram) was first extracted with a little acid, then thoroughly washed with hot water, rinsed back into the dish, and digested with hydrochloric acid of about 1.10 sp. gr. under varying conditions.

a. Digested twenty-five minutes on steam-bath with about 25 cc. acid. Silica in filtrate 0.0029 gram.

b. Same silica further treated as in *a* for one and one-half hours. Silica in filtrate 0.0026 gram.

c. Same silica gently boiled in platinum for thirty minutes with above acid. Silica in filtrate 0.0022 gram.

There was thus extracted with ease nearly 1.2 per cent. of the total silica without counting the probably larger amount held by the original filtrate, and it is to be presumed that the effect of the boiling would have been greater had it preceded instead of followed the quiet digestion.

It is thus plain how a portion of the silica always found in the filtrates gets there and that it is hopeless to try to prevent this by a single prolonged drying. Once the bulk of the silica is removed by filtration, however, then, after a second evaporation, because of its tendency to collect in clots of sensible size and consequent small surface exposure, the amount of silica going into solution is very small and by no means in proportion to that of the acid used.

DETERMINATION OF SILICA THAT HAS ESCAPED SEPARATION BY THE USUAL PROCESSES OF DEHYDRATION.

I pass now to another phase of the determination of silica, which so far as I am aware, has never been investigated.

While it has long been known that some silica passed into the filtrate in silicate work, it was supposed to be recovered in the ordinary course of analysis with the ammonia or basic acetate precipitate, whence after ignition and weighing it could be obtained in insoluble form by fusing the mixture with potassium pyrosulphate. I purpose showing that these suppositions are both in part erroneous, that the residual silica is, as Lindo says,[1] not

[1] Lindo (*Chem. News*, **60**, 14 (1889)) gives no quantitative data and in all his experiments (with glass) the ammonia precipitates were, of course, very small. It is fair to conclude from his addition of ferric chloride to the filtrates from them in order to recover by its precipitation by ammonia the "last trace" (*loc. cit.*, p. 40) of silica, that he would not have suspected the presence of any silica in these filtrates when analyzing mixtures containing considerable aluminum or iron oxide. Lindo's observations are of value, but his analytical results are not, for the reason that he operated largely in glass vessels and his alkaline solutions remained long in contact with glass, hence must have taken silica from them, notwithstanding which his analyses show without exception a large loss.

wholly precipitated by ammonia, and that the ordinary treatment of the pyrosulphate fusion mass recovers but a minor part of that which was thrown down with the oxides of iron and aluminum.

The experiments of the following table were made with a hydrochloric solution containing 0.0101 gram of silica in 10 cc. and with a solution of aluminum chloride free from silica. The amounts used were chosen to represent approximately the conditions most frequently prevailing in silicate analysis after but a single evaporation to separate silica. Precipitation was effected by ammonia at boiling temperature in a solution of about 300–400 cc. volume containing 25 cc. hydrochloric acid of 1.10 sp. gr. As soon as settled the alumina was filtered, washed, ignited, and fused with potassium pyrosulphate free from silica. The fused mass was generally dissolved in hot water acidulated with sulphuric acid, and once in warm water only, and the residual silica was collected, weighed, and corrected by hydrofluoric acid. In two cases (8 and 9) the filtrates were evaporated with excess of sulphuric acid, heated till fumes came off in quantity, and the separated silica collected after cooling and dilution of the solution. The filtrates from the alumina were evaporated, ignited to remove ammonium chloride, and the silica recovered by evaporation with a few drops of hydrochloric acid and further treatment as usual.

TABLE IV. SILICA IN ALUMINA AND IN FILTRATE FROM ALUMINA AFTER ONE PRECIPITATION BY AMMONIA.

	Al_2O_3 used.	SiO_2 used.	SiO_2 in filtrate.	SiO_2 recovered from Al_2O_3.	SiO_2 recovered from $K_2S_2O_7$ solution.
1.....	0.19	none	none	none	....
2.....	0.19	0.0101	....	0.003	....
3.....	0.19	0.0101	....	0.0037	....
4.....	0.19	0.0101	0.0020	....	....
5.....	0.19	0.0101	0.0021	....	....
6.....	0.19	0.0101	0.0007	0.0034	....
7.....	0.19	0.0101	0.0019	0.0021	....
8.....	0.20[1]	0.0101	0.0007	0.0033	0.0060
9.....	0.19	0.0101	0.0021	0.0023	0.0058

Treatment of about 0.01 gram of ignited precipitated silica with fused pyrosulphate resulted in the solution of 2 mg. of it and of 2.2 mg. in another test. Not being evenly distributed through a mass of other oxides undergoing solution the solvent

[1] Fe_2O_3.

effect of the pyrosulphate in these cases may reasonably be supposed to be less than in the tests of the table.

We here see how in practically all ordinary silicate analyses a portion of the silica, sometimes very small, escapes being weighed at all, since it mostly passes on into the filtrate from the magnesia. When a double precipitation by ammonia or sodium acetate is made, instead of one as in the above tests, the loss will be greater than the table shows.

We further see how, when correction is made for the silica with the alumina, it is only in small part recovered and the alumina is consequently made to appear too high when determined indirectly. Here we have an added argument in favor of endeavoring to collect all silica at the outset, for it is shown that the expectation of recovering the whole of a missing portion later is based on erroneous assumptions. Therefore Gilbert's conclusion, because he found very little silica with the alumina after fusion with pyrosulphate, that there is "no tendency for silica to recombine with the lime and alumina" (in non-magnesia silicates) "even at a temperature of 280° C."[1] is perhaps not well founded. Since his further conclusion that silica is almost completely dehydrated at 120°[2] is based on this same reason, his analytical results lose much of their value.

As showing the errors in the silica results that may be incurred in the analysis of certain siliceous ores where potassium pyrosulphate is employed as the means for breaking them up, I will here give the figures for two titaniferous magnetites. The lower values give the silica obtained in the usual way from the mixture of silica and silicates left after fusion with pyrosulphate, and the higher those afforded by direct fusion of the ores with sodium carbonate.

	I.	II.
Silica	11.73	20.82
	12.42	21.42

Complete analysis of the ores showed such a deficiency when pyrosulphate was used that the cause was sought and found to be as stated above. It was this observation which led to a portion of the work summarized in Table IV.

[1] *Technology Quarterly*, **3**, 63 (1890).
[2] *Loc. cit.*, p. 64.

THE PROPER TEMPERATURE FOR IGNITION OF SILICA.

Most authorities, Fresenius included, have directed that blast temperatures be used in order to obtain the correct weight of ignited silica. It is only recently that doubt has arisen as to this because of the experiments of Lunge and Millberg,[1] who, employing silica derived from silicon tetrafluoride, observed no further loss in weight over the blast after sufficient exposure to the full flame of a good Bunsen lamp. This was in direct conflict with all my experience in silicate work, and as a result of friendly correspondence Professor Lunge caused the matter to be reinvestigated in his laboratory a year ago and sent me the following table of results, which I take the liberty of making public.

TABLE V.—LOSS IN WEIGHT OF PURE SILICA FROM SiF_4, AT DIFFERENT TEMPERATURES AS DETERMINED BY DR. LOHÖFER, IN PROFESSOR LUNGE'S LABORATORY.

Temperature.	Time. Minutes.	*a.*	*b.*	*c.*
105°	..	0.1840	0.1778	0.2020
Dark redness	30	0.1643	0.1584	0.1803
Dark redness	30	0.1640	0.1584	0.1800
Full flame of burner	30	0.1622	0.1566	0.1779
Full flame of burner	30	0.1620	0.1564	0.1778
Blast	30	0.1619	0.1564	0.1776

It is but natural that Professor Lunge should write: "From these results I must conclude that Millberg and myself were right."

The following two tests by myself on silica similarly obtained confirm the above, and show, after blasting, further slight losses comparable with those appearing in Professor Lunge's table and of the same order as those produced by more than half an hour's blasting with silica precipitated by acid (see Table VIII).

TABLE VI.—SHOWING LOSS IN WEIGHT OF PURE SILICA FROM SiF_4, ACCORDING TO TESTS MADE BY MYSELF.

	a.
	0.5053
Full burner flame 30 minutes	0.5017
Blast flame 30 minutes.....	0.5014
	b.
	0.5030
Full burner flame 45 minutes	0.4997
Full flame 45 minutes	0.4995
Blast flame 40 minutes.....	0.4991[2]

[1] *Ztschr. angew. Chem.*, p. 425 (1897).

[2] This loss is partly chargeable to the crucible itself.

These slight losses are not due to mechanical carrying off of silica, for the latter had utterly lost its extraordinarily down-like character during the early heating and become converted by the blasting into a coherent cake of enormously reduced bulk.

Let me now, however, present another series of results furnished by silica otherwise precipitated. The silica used was obtained by three evaporations from the quartz that served for the earlier experiments of this paper, and the initial weights are those found after an exposure of about one hour to the full Bunsen flame. The weights given represent the silica as corrected by hydrofluoric and sulphuric acids for the few tenths of a milligram of non-volatile salts always present. The crucibles were found not to lose weight themselves over the blast. The quartz powder employed was 99.88 per cent. pure, as found by careful evaporation with hydrofluoric and sulphuric acids.

TABLE VII.—SHOWING DIFFERENCES IN WEIGHTS OF SILICA PRECIPITATED FROM SODIUM SILICATE WHEN IGNITED OVER BUNSEN BURNER AND BLAST-LAMP.

No.	Weight of quartz.	Silica found.		Loss in weight.	Percentages found.	
		Burner 1 hr.	Blast ½ hr.		Burner.	Blast.
1	0.5738	0.5761	0.5735	0.0026	100.40	99.95
2	0.5931	0.5945	0.5930	0.0015	100.24	99.98
3	0.6401	0.6450	0.6394	0.0056	100.76	99.90
4	0.6638	0.6668	0.6628	0.0040	100.45	99.85
5	0.7028	0.7058[1]	.....	.....	100.25	....
6	0.7309	0.7342	0.7306	0.0036	100.45	99.96
7	0.8208	0.8271	0.8206	0.0065	100.77	99.98
8	0.8495	0.8521	0.8484	0.0037	100.31	99.88
9	0.8943	0.8996	0.8936	0.0060	100.59	99.92
10	.....	0.9989	0.9898	0.0091	.....	....

Results similar to the above are repeated in every silicate analysis that is made in our laboratory, and others have told me their experience is the same. It is as clear as daylight that the blast is a necessity if the work is to be at all accurate. In every one of the above instances the percentage found without blast is far in excess of 99.88, the true value for silica in the quartz, and is as invariably brought very near this value and with far smaller variations from a mean when the blast is applied (see further, p. 373). The above values for "burner" percentages very well represent the usual lack of exact agreement in series of duplicate silica determinations, when the blast has not been used (see Gil-

[1] Two hours.

bert's paper), while those of the next column show of what accuracy the determination is susceptible when all the conditions of success are understood and applied.

From the foregoing it appears that the silica separated by water from silicon tetrafluoride and that by hydrochloric acid from sodium silicate are in different conditions and behave differently when strongly heated; that Professor Lunge's conclusion that silica need not be blasted, while correct for one form of silica, cannot be applied, as he supposed, in analytical work.

I have always, until lately, regarded one-half hour's blasting as sufficient in all cases for as much as a gram of silica, but that this length of time is often insufficient to secure constant weight is indicated by some of the results in Tables V and VI and still more by those in the following:

TABLE VIII.—SHOWING NEED OF VERY LONG BLASTING AT TIMES.

Heat.	Time in minutes.	Weights of silica. 1.	2.	3.	4.	5.	6.
Burner	60	0.6691	0.7041	0.9989	.....	0.4175	0.4220
Blast	30	0.6657	0.6982	0.9905	0.7208	0.4154	0.4192
Blast	30	0.6656	0.6979	0.9902	0.7201	.....	0.4187
Blast	30	0.6651	.....	0.9899	0.7193	0.4152	0.4185
Blast	30	.....	.....	0.9897	0.7194	.....	.....
Blast	30	.....	.....	.....	0.7194	.....	.....

The progressive losses shown here are not chargeable to the crucibles, nor were they due to mechanical loss of silica or to volatilization of included salts, and they explain very well the fact that nearly all the figures of the first column in Table V slightly exceed the true value for silica in the quantity used, for they were obtained by blasting for only one-half hour. They may also serve to explain in small part the excessive summations often encountered in rock analyses. These later losses can exert little effect when the silica percentages are small, but when large, as in rock analysis, they may at times be of moment and necessitate blasting for more than half an hour.

In the foregoing I have entered into such detail as the exact scientific worker needs for his enlightenment and have carried my separations and ignitions farther than the technical chemist ordinarily cares to or can proceed. But in its main features, what I have said concerns him not less than the research chemist and I trust that in some respects it may help to ease his path.

SUMMARY.

Statements of earlier writers are fully confirmed, that silica cannot be rendered wholly insoluble by a single or any number of evaporations with hydrochloric acid when followed by a single filtration, no matter what temperature may be employed, but that two or more evaporations alternating with filtrations are necessary to secure satisfactory results.

It is shown that the generally accepted view that any silica passing into the filtrate is wholly thrown down by ammonia or sodium acetate in presence of much aluminum or iron is incorrect. Also that silica is appreciably soluble in melted potassium pyrosulphate and that consequently when siliceous oxides of iron and aluminum obtained in analysis are then fused their silica contents are only in small part left undissolved when the fused mass is taken up with water or acid. Both these sources of error are avoided by separating all silica at the start as above.

The need of blast ignition in order to get the correct weight of silica obtained in analysis is proved. The opposite conclusion of Lunge and Millberg, being based on what seems to be a different behavior of the silica derived from silicon tetrafluoride, is therefore not justified.

LABORATORY U. S. GEOLOGICAL SURVEY,
December, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REDETERMINATION OF THE ATOMIC WEIGHT OF CALCIUM—PRELIMINARY PAPER.

BY THEODORE WILLIAM RICHARDS.

Received February 16, 1902.

DURING the years 1897 to 1899 an investigation upon the atomic weight of calcium was conducted in the Chemical Laboratory of Harvard College. This investigation was more carefully conducted, and in some respects more elaborate than any previous research of a similar kind conducted in this laboratory. The details are so many that time has not yet been found for a verbal presentation of them, but a brief report of the results was made to the American Association for the Advancement of Science in August, 1899, of which a notice is published in the journal.[1]

[1] This Journal, **22**, 72 (1900).

Very recently there has appeared the account of a careful investigation of calcium carbonate made by Hinrichsen under the direction of Landolt.[1] Since this investigation confirms the outcome of the Harvard research, a brief preliminary account of this may be interesting. It is hoped that later the details may be presented in full.

In spite of the common occurrence of the element calcium, its atomic weight had been investigated only in a partial and incomplete manner. The chief work upon the subject has consisted of the quantitative ignition of calcium carbonate, and it seemed important to obtain also data of a radically different kind. Because of the peculiar properties of the halides of silver, most of the accurately determined atomic weights of other metals have been found by the analysis of their respective halides, and it would evidently be worth while to include calcium in this series. The old work of Dumas is, of course, of no importance, because of his faulty comprehension of the method of Gay-Lussac.

Accordingly the present series of determinations consisted of the analysis of calcium chloride, the silver chloride obtained from a known weight of the anhydrous salt being collected and weighed with care.

The first problem to be solved was the preparation of pure calcium chloride. Preliminary experiments showed that calcium nitrate is the best salt to use for recrystallization, because of its rapid variation of solubility with the temperature, and because of the fact that the corresponding salts of magnesium, strontium, and barium do not crystallize out with it. Two portions of marble were used as the starting-point, one came from Rutland, Vermont, U. S. A., while the other was a specimen of the purest Italian marble taken from a ship which had just arrived at the port of Boston. The Rutland marble was converted into the nitrate, and from this specimen, after preliminary purification with lime, etc., two samples were prepared, one having been carefully recrystallized ten times, and the other twenty times.[2]

The single specimen of pure nitrate from the Italian marble was recrystallized fifteen times, thus being comparable with the

[1] *Ztschr. phys. Chem.*, **39**, 311 (1901).

[2] The process of recrystallization was kindly conducted by M. J. B. Churchill, who also made the preliminary experiments, showing the degree of purity to be obtained in this way.

average of the American samples, in case any difference between them might exist.

The metal in each of these specimens was precipitated as carbonate by the purest ammonium carbonate, and then converted into chloride. After four recrystallizations the chloride was dried, ignited in a porcelain tube in a stream of hydrochloric acid gas to render a possible trace of silica insoluble, dissolved, filtered, and crystallized twice more. Of course platinum vessels were used throughout, and every precaution was taken to insure a close approach to that perfect purity which is unattainable.

The three samples of material which had been thus made ready were dried for analysis by prolonged ignition and final fusion at a bright red heat in a porcelain tube. The hydrochloric acid gas, which had been added to the nitrogen in the tube to prevent loss of chlorine, was then wholly displaced by the inert gas, and when the apparatus was nearly cold this was driven out by dry air. After having been transferred to the stoppered weighing-bottle by means of the convenient automatic bottling apparatus so much used at Harvard, it was weighed and analyzed. The correction for the solubility of the silver chloride was determined much as in the case of barium chloride, several years ago.

The results show that the three samples of calcium chloride (which were wholly neutral to methyl orange) were essentially identical. Hence neither a change in the source of the material nor repeated fractionation causes any variation in the atomic weight. The following table contains the weights of material, reduced to the vacuum standard, and the calculated results.

THE ATOMIC WEIGHT OF CALCIUM.

O = 16.000; Cl = 35.455.

No.	Weight of $CaCl_2$ in vacuum.	Weight of AgCl in vacuum.	Atomic weight of calcium.
1	1.56454	4.0409	40.121
2	3.57630	9.2361	40.130
3	3.59281	9.2788	40.129
4	5.00880	12.9364	40.124
5	9.00246	23.2506	40.125
		Average,	40.126
American (10 crystallizations), Nos. 2, 5			40.127
American (20 crystallizations), No. 4			40.124
Italian (15 crystallizations), Nos. 1, 3			40.125

The results thus agree closely with the value 40.142 since obtained by Hinrichsen, who was not cognizant of my work. A further investigation is now being undertaken at Harvard to show whether other methods, executed with great care, support or discountenance this high value.

COMMERCIAL AQUA AMMONIA, ITS EFFECT UPON IRON, ITS IMPURITIES, AND METHODS FOR DETERMINING THEM.

By J. D. Pennock and D A. Morton.

Received January 10, 1902.

THE very extensive development of refrigerating plants, large and small, throughout the country during the last decade has greatly increased the manufacture of aqua ammonia.

Formerly aqua ammonia of 26° Bé., or 29.0 per cent. NH_3, was shipped in carboys. The shipments of aqua soon became so large that it was no longer practicable to transport in such cumbersome and fragile receptacles, and recourse to metal carriers was had. But ammonia was known to attack most metals seriously. W. R. Hodgkinson and N. E. Bellairs[1] found that all metals which form soluble double salts with ammonium salts are most acted upon by ammonia solution. Zinc, nickel, and cobalt are, after copper, most rapidly attacked. Lead dissolves more slowly, and iron, aluminum, and magnesium do not appear to dissolve at all.

Lunge says[2] that aqua ammonia in contact with iron, "gives rise to red precipitates of iron oxides."

Lunge's opinion was evidently held by European ammonia manufacturers, for in one of the larger works that the writer visited in Belgium in 1897, the absorber for the ammonia gas was a lead-lined vessel, and the aqua produced was shipped in carboys.

The opinion was held by certain manufacturers that aqua made from the distillation of sulphate of ammonia with lime would not attack iron, but that aqua made from crude ammonia liquor would.

To ascertain the effect of ammonia on iron and determine if an iron absorber could be used in place of a lead one, and if aqua could be shipped in iron drums and iron cars, various experiments

[1] *Proc. Chem. Soc.*, **9**, 146 (1895).

[2] "Coal-Tar and Ammonia," p. 685.

were undertaken. In these experiments, (1) absolutely C. P. aqua, made from C. P. sulphate, distilled with C. P. lime into distilled water, (2) the ordinary commercial aqua, made from sulphate, and (3) several samples, containing different percentages of impurities, all made from the direct distillation of crude liquor without first forming the sulphate, were used.

To ascertain the effect of these different ammonia solutions upon iron, small bottles, 7 inches high and 1.5 inches in diameter, were partly filled with the ammonia solution, and a bright nail, carefully cleaned by filing, was introduced into the solution, and left in contact with it twenty-four hours before examination.

The composition of the ammonia solutions used was:

1. Practically chemically pure aqua, containing 28 per cent. NH_3.

2. Aqua from sulphate, containing organic matter equivalent to 10 cc. centinormal potassium bichromate per 100 cc. aqua, 0.046 gram per liter carbon dioxide, no chlorine, no sulphate, 2 grams per liter pyridine, and 28.5 per cent. NH_3.

3. Thirteen samples of aqua from crude liquor containing organic matter equivalent to from 5 to 80 cc. potassium dichromate, carbon dioxide from 0.1 to 2 grams per liter, chlorine 0.0 to 0.1 gram per liter, and pyridine, 0.1 to 5 grams per liter, and 28.5 per cent. NH_3.

Upon examining the samples after exposing twenty-four hours, it was found that the C. P. aqua, that made from sulphate, and eight of those made from crude liquor, remained perfectly clear, and the iron was in no way acted upon; but that five were badly attacked, the nail being decidedly rusty, and the solution cloudy with reddish yellow oxide, very finely divided, which remained in suspension and would not settle. It was thought the nails had not been perfectly cleaned, because the composition of the ammonia solutions was so slightly different; five other nails were put into fresh solutions of the same kind, and after twenty-four hours all remained perfectly bright, and the solutions perfectly clear, showing that metallic iron, if perfectly free from specks of rust, is unattacked by strong solutions of ammonia, even if these solutions contain 2 grams per liter carbon dioxide, 5 grams per liter pyridine, and a high percentage of organic matter.

But, of course, it is impossible to so treat the inside of an iron absorber, a drum or tank, that its surface shall be entirely free

from rust, and consequently when one begins to make aqua ammonia in an iron absorber, or ship it in drums or tank cars, reddish precipitates of iron oxide, which settle with great difficulty, are formed.

Further experiments with iron nails in different stages of oxidation were made with the same solutions, and it was found that a nail freshly rusted forms immediate and continued discoloration of the aqua, while a nail with a thick coating of old rust completely covering the iron does not influence the ammonia solution in the slightest degree.

To be able therefore to absorb strong ammonia solution in an iron vessel, or to ship it in drums or tank cars, it is necessary in some way to coat the surface of the iron with an oxide. This is not an easy matter. Boiling the drum in a weak solution of permanganate of potash will do it, but this is expensive. It has been found, from experiment, however, that by continuous use of the iron absorber, or by repeatedly shipping in drums or cars, this desirable coating is formed, and the aqua is finally not discolored. In the language of the factory, the tank becomes "seasoned," and when this has taken place there is no further trouble from discoloration by iron oxides.

For the rusting of iron it is necessary that water, carbon dioxide, and oxygen, must come in contact with the metal.

The reactions illustrating its formation are:

$$Fe + 2H_2CO_3 = \underset{\substack{\text{Ferrous acid}\\ \text{carbonate.}}}{FeH_2(CO_3)_2} + 2H.$$

$$H_2 + O = H_2O.$$

$$2FeH_2(CO_3)_2 + O = Fe_2O_3 + 4CO_2 + 2H_2O.$$

Only traces of carbon dioxide and water are necessary to cause continuous rusting.

In the above reaction it is free carbonic acid that reacts with the iron. In ammonia solutions there can be no free carbonic acid, as all carbon dioxide, even in the air above the liquid, is present as ammonium carbonate. It seems quite possible that the weak affinity of iron for carbonic acid would not be sufficient to remove the latter from ammonium carbonate; in other words, it is only free carbonic acid that is available for rusting iron.

All of our experiments with aqua have verified the following conclusions:

A. Concentrated aqua not only does not rust *clean* iron, but it actually prevents its rusting, even in the presence of water, oxygen, and ammonium carbonate. This conclusion indicates that *free* carbonic acid is necessary in the rusting of iron.

B. If iron, freshly rusted and still moist, be treated with concentrated aqua, the rusting continues for a considerable length of time. In this case we have iron coated, presumably, with more or less ferrous acid carbonate, $FeH_2(CO_3)_2$. This gives off free carbon dioxide and water in contact with the iron, and even in the strong aqua solution the rusting may be indefinitely continued by means of this very small amount of carbon dioxide.

C. Iron, which has been rusted for a considerable time, is not affected by concentrated aqua. The iron here is coated with ferric oxide and not ferrous acid carbonate, so there is no carbon dioxide available to cause further rusting.

The impurities to be found to a greater or less degree in aqua ammonia are carbon dioxide, tarry organic matter, pyridine, and seldom, if ever, hydrogen sulphide.

CARBON DIOXIDE.

The two methods which we have found to be best adapted for the determination of the small percentage of carbon dioxide in aqua are what may be termed the "precipitation" and the "direct titration method." The latter is the best, being the most accurate, as well as the most rapid.

Precipitation Method.—To 100 cc. aqua ammonia, in a suitable flask,[1] add 5 cc. normal sodium hydroxide,[2] and boil until the bulk of the solution is reduced to about 20 cc.[3] While still hot add 5 cc. barium chloride solution, drop by drop, and with constant shaking, filter immediately and quickly by suction, and wash the flask and filter five times, using about 10 cc. of water for each washing.[4] Return the precipitate and filter to the flask, add excess of fifth-normal sulphuric acid, boil to remove carbon

[1] A conical flask of about 300 cc. capacity is most convenient.

[2] The amount of carbon dioxide in 5 cc. of the normal sodium hydroxide must be determined and allowed for in the aqua analysis.

[3] By boiling down, all ammonia is removed, and all carbon dioxide retained as sodium carbonate.

[4] The object of the washing is to remove all traces of sodium hydroxide. The wash-water must be neutral and free from carbon dioxide, but should contain phenolphthalein, so as to carry out the removal of sodium hydroxide intelligently. The filter will still be slightly pink after washing five times, but this number has been found to give best results. Further washing dissolves barium carbonate and gives too low results.

dioxide and titrate back with fifth-normal sodium hydroxide, using phenolphthalein as an indicator.

1 cc. N/5 NaOH = 0.0044 gram CO_2.

No. of cc. N/5 H_2SO_4 — cc. N/5 NaOH × 0.044 = grams per liter of CO_2 in the aqua tested.

The accuracy of this method was tested as follows:

I. 100 cc. of an aqua to which ammonium carbonate had been added was neutralized and the carbon dioxide present very carefully determined by absorption and weighing in the usual way.

Result: 100 cc. aqua contained 0.1253 gram carbon dioxide, which, for 25 cc. aqua would be 0.0313 gram carbon dioxide.

By the Precipitation Method.—(1) 25 cc. aqua contained 0.0315 gram carbon dioxide; (2) 25 cc. aqua contained 0.0317 gram carbon dioxide.

II. Tests by this method, omitting the evaporation of solutions containing a known amount of sodium carbonate, resulted as follows:

Carbon dioxide contained, gram.	Carbon dioxide found, gram.
0.0042	0.0042
0.0042	0.0044
0.0084	0.0079
0.0084	0.0081
0.0084	0.0092
0.0084	0.0088
0.0168	0.0169

III. Duplicate determinations, by this method, on 20 samples of aqua, have agreed in every case (with one exception) within 0.001 gram carbon dioxide per 100 cc. aqua.

Direct Titration Method.—1. To 100 cc. of the aqua, contained preferably in a 300 cc. conical flask, add 5 cc. normal sodium hydroxide and boil until the bulk of the solution is reduced to about 20 cc.

2. To this residue add 50 cc. of water (neutral, free from carbon dioxide and containing phenolphthalein), cool to 10° C., and bring to the neutral point by adding: first, normal sulphuric acid until the end point is nearly reached; next, tenth-normal sulphuric acid until the last trace of pink is just removed. *Excess of sulphuric acid must not be present at any time during this neutralization.*

3. To the solution thus neutralized add a measured quantity of tenth-normal sulphuric acid (usually 10 cc.), boil two

minutes to remove carbon dioxide, cool, and titrate back with tenth-normal sodium hydroxide.

(No. of cc. N/10 H_2SO_4 — cc. N/10 NaOH) × 0.044 = grams per liter CO_2 in the aqua.

The carbon dioxide contained in 5 cc. normal sodium hydroxide must be determined and allowed for in the aqua analysis.

Concerning the respective steps of this analysis the following facts may be noted:

1. When aqua ammonia is boiled down in the presence of sodium hydroxide all carbon dioxide is retained as sodium carbonate, even though the evaporation be carried nearly to dryness. The purpose of boiling down with sodium hydroxide is to remove all ammonia, to reduce the bulk of the solution, and to retain all carbon dioxide as sodium carbonate.

2. The addition of acid as described, will set free a little carbon dioxide which may partially volatilize from the solution if the latter be too concentrated. By dilution with 50 cc. of water, this cause of error is averted.

Before bringing to the neutral point the solution must be cooled to a low temperature (below 10° C.), otherwise the phenolphthalein color end point is not sufficiently distinct. Also there is less liability of loss of carbon dioxide by too rapid addition of acid, if the solution be well cooled.

The end-point is just reached when sufficient acid has been added to convert all the sodium carbonate into sodium bicarbonate, since the former is alkaline and the latter neutral to phenolphthalein. This neutralization is represented by the equation:

$$2Na_2CO_3 + H_2SO_4 = Na_2SO_4 + NaHCO_3.$$

Excess of sulphuric acid must not be present at any time during this neutralization, because it will almost certainly cause a loss of carbon dioxide before excess of alkali can again be added.

3. The final step is the decomposition of the sodium bicarbonate by addition of an excess of sulphuric acid, the removal of carbon dioxide by boiling, and the titration of the excess of sulphuric acid by alkali.

$$\underset{168}{2NaHCO_3} + \underset{98}{H_2SO_4} = Na_2SO_4 + 2H_2O + \underset{88}{2CO_2}.$$

One cc. tenth-normal sulphuric acid (0.0049 gram sulphuric acid) sets free 0.0044 gram carbon dioxide.

Hence:

(No. of cc. N/10 H_2SO_4 — cc. N/10 NaOH) × 0.0044 = grams CO_2 in 100 cc. aqua.

RESULTS.

TESTS WITH SODIUM CARBONATE SOLUTIONS CONTAINING A KNOWN AMOUNT OF CARBON DIOXIDE.

Carbon dioxide contained. Gram.	Carbon dioxide found by direct titration method. Gram.
0.0042	0.0042
0.0084	0.0080
	0.0085
	0.0087
	0.0078
	0.0080
	0.0085
	0.0080
0.0168	0.0166
	0.0161
	0.0164
0.0084	0.0088
	0.0086

The last two determinations were made at night, by the light of incandescent lamps.

A large number of determinations of carbon dioxide in aqua by this method, and a comparison of its results, on the same aquas, with those obtained by the precipitation method, have fully confirmed its accuracy.

CONCLUSIONS.

From the results obtained the conclusion is reached that the direct titration method for carbon dioxide in aqua ammonia is, all points considered, the best. It is accurate, rapid, and simple.

Equally accurate results can scarcely be obtained by the precipitation method, and the direct titration method requires less careful manipulation, takes less time, and avoids the liability to error which is occasioned by precipitation and washing of the barium carbonate. On the other hand in using the direct titration method, sulphides, if present, must be removed before making the titrations, while this removal is unnecessary in the case of the precipitation method.

Tarry organic matter, as found in ammonia, is best determined by oxidation with potassium bichromate instead of potassium permanganate, which in the cold does not completely oxidize, and at boiling temperature is itself decomposed, whereas potassium bichromate does not undergo decomposition, and with its use check results may be obtained even at different times of boiling. The method was devised by Mr. J. G. Hazard, and is the one we have adopted.

Potassium permanganate affects pyridine slightly, but by no means entirely oxidizes it. We therefore prefer to make a test for the organic matter with potassium bichromate which does not oxidize pyridine at all, and then make a separate determination of the pyridine. The method is as follows:

DETERMINATION OF ORGANIC MATTER IN AQUA AMMONIA.

Make up fiftieth-normal solutions of ammonium sulphate, ferrous sulphate, potassium permanganate, and potassium bichromate.

Introduce 10 cc. of aqua (from pipette) into a 300 cc. Erlenmeyer flask, add 20 cc. fiftieth-normal potassium bichromate solution (from burette), and 50 cc. dilute sulphuric acid (1 : 3). Heat to boiling and boil gently for about twenty minutes, adding distilled water if necessary to keep the volume above 50 cc. After boiling, cool to temperature of the room and add fiftieth-normal ammonium ferrous sulphate solution (from burette) in excess, and titrate back to faint pink color with fiftieth-normal potassium permanganate. The pink color will always fade out in a short time.

Add number of cubic centimeters potassium permanganate used, to number of cubic centimeters potassium bichromate used, and subtract number of cubic centimeters ammonium ferrous sulphate used. Deduct number of cubic centimeters potassium bichromate used up in a blank sample, and report result as number of cubic centimeters centinormal potassium bichromate used per 100 cc. aqua.

The end-point of the method appears to be perfectly definite, no further oxidation occurring by boiling considerably longer than the prescribed twenty minutes. The results obtained have indicated that all organic coloring-matter, or compounds which may change over into colored products are determined by this

method, while pyridine, and perhaps other stable organic bodies, are unattacked. A sample of aqua to which pure pyridine had been added gave almost exactly the same result as it gave by a test before the addition.

PYRIDINE.

Pyridine in aqua to be used in making liquid ammonia causes much trouble in the compressors and must be kept down to a low figure.

For the detection of traces of pyridine in commercial ammonia, "H. Ost recommends that the sample should be nearly neutralized when the odor of pyridine may be recognized. By distilling the nearly neutralized liquid, collecting the distillate in hydrochloric acid, evaporating, and extracting the residue with absolute alcohol, a solution is obtained containing but little ammonium chloride. What is present is removed by boiling off the alcohol and adding platinic chloride solution when, on evaporating the filtrate and adding alcohol, the pyridine chloroplatinate crystallizes in smooth, ramifying, orange-red prisms, readily soluble in boiling, but very sparingly in cold water."

But this is only a qualitative determination, while the following method gives excellent results quantitatively:

DETERMINATION OF PYRIDINE IN AQUA AMMONIA.

100 cc. of the aqua are nearly neutralized with sulphuric acid (1 : 5), keeping the mixture moderately cool meanwhile, so that pyridine will not be volatilized. Finally, cool to 20° C., add 1 or 2 drops of methyl orange and bring exactly to the neutral point with normal acid and alkali.

This neutral mixture is then placed in a suitable distilling flask and distilled until 70 cc. have passed over, the distillate being collected in 30 cc. of cold water contained in a small receiver.

Unless the aqua contains an unusually large amount of pyridine (*i. e.*, over 2.5 grams per liter), the 100 cc. of liquid now in the receiver contain *all the pyridine* which was present in the aqua and a small amount of free ammonia. The amount of ammonia (NH_3) which is thus carried over will usually be equivalent to about 2 cc. normal solution.

Cool the contents of the receiver to below 10° C., add phenolphthalein, then, from a burette, mercuric chloride solution until

the last trace of pink is just removed, and finally 4 drops more of mercuric chloride solution to insure complete removal of the ammonia.

The mercuric chloride removes all the free ammonia according to the equation

$$HgCl_2 + 2NH_3 = \underset{\text{white precipitate}}{NH_2HgCl} + NH_4Cl.$$

Phenolphthalein is colored by free ammonia, but not by pyridine, so that the pink color of the solution is just removed when all the free ammonia has been acted upon.

The mixture is now filtered and the filtrate, containing pyridine bases alone, is titrated with normal sulphuric acid, after adding one drop of methyl orange for an indicator.

1 cc. normal H_2SO_4 = 0.079 gram pyridine.

RESULTS OF DETERMINATIONS OF KNOWN QUANTITIES OF PYRIDINE IN AQUA.

Grams per liter present...	1.16	2.16	4.16	2.2	1.16
" " " found	1.11	2.0	4.11	2.3	1.15

Water, to which a known quantity of pyridine was added, was carried through the method.

Grams per liter present.....	1.9
" " " found.....	1.9

In the manufacture of aqua it is a great convenience to know, without making an analysis, the percentage of ammonia in an aqua by simply taking the degree Baumé. The temperature of the manufactured article as it leaves the absorber, of course, varies slightly.

Having determined the percentage of ammonia in three samples of different strengths, we have found the degree Baumé of each at temperatures varying from 10° C. to 30° C., and after plotting these on a chart, we have worked up the following table, by which, at a glance, one may learn the percentage of ammonia in a given sample of aqua, having determined the temperature and degree Baumé.

In shipping strong aqua, 29 to 30 per cent., to a hot climate in tank cars, one must take into consideration the great expansion of ammonia at temperatures which are likely to prevail in the summer months, and see to it that his tank will withstand the pressure as, of course, the tank will be sealed up. The following

PER CENT. OF AMMONIA IN AQUA FOR TEMPERATURES BETWEEN 10° C. AND 30° C., AND ANY DEGREE BAUMÉ READING BETWEEN 24° AND 27°.

Bé.	10° C.	11° C.	12° C.	13° C.	14° C.	15° C.	16° C.	17° C.	18° C.	19° C.	20° C.	21° C.	22° C.	23° C.	24° C.	25° C.	26° C.	27° C.	28° C.	29° C.	30° C.
24.0	26.2	26.0	25.8	25.7	25.5	25.3	25.1	24.9	24.8	24.6	24.4	24.3	24.1	23.9	23.7	23.6	23.4	23.3	23.1	22.9	22.8
.1	.4	.2	26.0	.8	.7	.5	.3	25.1	25.0	.8	.6	.5	.3	24.1	.9	.8	.6	.4	.3	23.1	23.0
.2	.6	.4	.2	26.0	.8	.7	.5	.3	.2	25.0	.8	.7	.5	.3	24.1	24.0	.8	.6	.5	.3	.2
.3	.8	.6	.4	.2	26.0	.9	.7	.5	.4	.2	25.0	.9	.7	.5	.3	.2	24.0	.8	.6	.5	.3
.4	27.0	.8	.6	.4	.2	26.1	.9	.7	.5	.4	.2	25.1	.9	.7	.5	.4	.2	24.0	.8	.6	.5
.5	.2	27.0	.8	.6	.4	.3	26.1	.9	.7	.6	.4	.3	25.1	.9	.7	.5	.4	.2	24.0	.8	.7
.6	.4	.2	27.0	.8	.6	.5	.3	26.1	.9	.7	.6	.5	.3	25.1	.9	.7	.6	.4	.2	24.0	.9
.7	.6	.4	.2	27.0	.8	.7	.5	.3	26.1	.9	.8	.6	.5	.3	25.1	.9	.7	.6	.4	.2	24.0
.8	.8	.6	.4	.2	27.0	.9	.7	.5	.3	26.1	26.0	.8	.6	.5	.3	25.1	.9	.7	.6	.4	.2
.9	28.0	.8	.6	.4	.2	27.1	.9	.7	.5	.3	.2	26.0	.8	.6	.5	.3	25.1	.9	.7	.6	.4
25.0	.2	28.0	.8	.6	.4	.3	27.1	.9	.7	.5	.4	.2	26.0	.8	.6	.5	.3	25.1	.9	.7	.6
.1	.4	.2	28.0	.8	.6	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8	.6	.5	.3	25.1	.9	.7
.2	.6	.4	.2	28.0	.8	.7	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8	.6	.5	.3	25.1	.9
.3	.8	.6	.4	.2	28.0	.9	.7	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8	.6	.5	.3	25.1
.4	29.0	.8	.6	.4	.2	28.0	.9	.7	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8	.6	.5	.3
.5	.2	29.0	.8	.6	.4	.2	28.0	.9	.7	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8	.6	.5
.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.9	.7	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8	.7
.7	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.5	.3	27.1	.9	.7	.6	.4	.2	26.0	.8
.8	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.1	.9	.7	.6	.4	.2	26.0
.9	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.1	.9	.7	.6	.4	.2
26.0	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.1	.9	.7	.6	.4
.1	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.1	.9	.7	.5
.2	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.1	.9	.7
.3	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.1	.9
.4	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2	27.0
.5	.2	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4	.2
.6	.4	.2	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6	.4
.7	.6	.4	.2	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8	.6
.8	.8	.6	.4	.2	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0	.8
.9	32.0	.8	.6	.4	.2	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2	28.0
27.0	.2	32.0	.8	.6	.4	.2	31.0	.8	.6	.4	.2	30.0	.8	.6	.4	.2	29.0	.8	.6	.4	.2

table shows the pressure developed by strong ammonia solutions exposed to different temperatures:

PRESSURE PRODUCED BY EXPOSING AQUA AMMONIA TO DIFFERENT TEMPERATURES.

The apparatus in which this test was made consisted of a cast-iron fitting piece with a pressure gauge and a mercury gauge attached. The relation of the liquor to the unoccupied space of the apparatus was the same as the relation of liquor in a tank car to the unoccupied space of the car. The apparatus was set in a water tank which was heated externally, and readings of the pressure gauge end of the mercury gauge made at every degree of temperature. The thermometer was placed in the aqua.

Experiment was carried to 120.2° F.

The rate of heating was 1° every six minutes.

The percentage of ammonia was 28.5, and the number of cubic centimeters aqua used was 2800.

°C.	°F.	Pounds pressure.	Inches mercury.	°C.	°F.	Pounds pressure.	Inches mercury.
23	73.4	2½	4½	37	98.6	10½	21¾
24	75.2	3	6½	38	100.4	11	22¾
25	77.0	4	7½	39	102.2	11½	23¾
26	78.2	4½	8¼	40	104	12	24¾
27	80.6	5	9¼	41	105.8	12½	25½
28	82.4	5	10¼	42	107.6	13	26¾
29	84.2	5	11¼	43	109.4	13½	27¾
30	86	6	12½	44	111.2	14	28¾
31	87.8	6½	13¾	45	113	14½	29¾
32	89.6	8	16	46	114.8	15	30¾
33	91.4	8	17½	47	116.6	15½	31¾
34	93.2	9	18¼	48	118.4	16	32¾
35	95	9½	19	49	120.2	16½	33¾
36	96.8	10	20½				

A NITROGEN APPARATUS.

By J. A. WESENER.

Received November 20, 1901.

THE purpose of this apparatus, as illustrated and described herewith in detail, is to secure greater rapidity in the ordinary nitrogen estimation. The method adopted in this apparatus for estimating nitrogen is by distilling the alkaline mixture in a current of steam, using the same steam which makes the

distilled water in the laboratory. This apparatus has been in constant use in the Columbus Laboratories since last March.

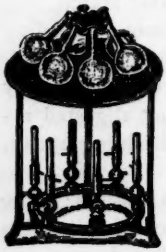
In point of accuracy, it is equal to the common prevailing method, while in rapidity it by far outclasses the old method. Ten minutes from the time the jet of steam is turned on is amply sufficient to expel all the ammonia in the product digested according to the official Kjeldahl method, and obtaining 250 cc. distillate in each flask.

The general description of the apparatus is as follows: The distillation flask is round-bottomed, and of 24 ounce capacity. In the neck of this flask is fitted a perforated rubber stopper, and flush with both ends a copper tube. To the upper end of this tube is fitted two hollow brass balls, the first and smallest being of about 40 cc., and the largest of 70 cc. capacity. Entering at the top of the first ball, and passing nearly to the bottom of the flask, is a thistle tube of glass, with a stop-cock. The object of this tube is to allow the alkali to be put in after the flask is connected with the condenser, and hence no ammonia is lost while connecting the apparatus.

From the side of the brass ball nearest the condenser leads a pipe of block tin tubing curving up to the second brass ball, which, as stated, is larger than the first. From this second ball a block tin tube leads again to the condensing coil, and is soldered in place at both ends. On the side of the first brass ball farthest from the condenser, at the junction of the ball with the tube, leading through the rubber stopper, is a small brass tube, 1/16 of an inch in diameter, with the joint at right angles, and joined to this is a glass tube which passes down below the surface of the liquid in the flask. Through this tube passes the steam for distillation. In the operation of the original apparatus, the steam is furnished from a boiler heated by steam coils, which is the source of the laboratory's distilled water.

In the apparatus as above described the operation is carried on as follows: The material is digested in a 24-ounce, round-bottomed flask, by using 15 cc. of concentrated sulphuric acid, plus a globule of mercury. After the digestion is complete, the flask is allowed to cool; is then diluted with distilled water, and connected to the apparatus. Sixty cc., which is the amount the cup in the thistle tube will hold, of 50 per cent. strength sodium hydroxide, is next added, the steam turned on, so as to mix the

alkali and acid, and then 20 cc. of the 4 per cent. potassium sulphide solution is added. The object of adding the potassium sulphide solution last is to avoid carrying over hydrogen sulphide in the distillate. The distillate is collected in ordinary 500 cc. flasks, in which a little distilled water is placed, so as to dilute the ammonia as it distils off.



I have found that no ammonia is lost by simply allowing the distillate to run in a flask containing distilled water, and therefore dispense with using standard acid solution. A trial of six ureas were digested according to the Kjeldahl method; three of the distillates were collected in decinormal sulphuric acid solution, and the other three were collected in distilled water, all titrated the same.

The steam pressure necessary to run a battery of six flasks briskly is 1 to 2 pounds. In case no steam is available in the laboratory, then a small copper boiler can be used, which being heated with one large gas-burner will furnish sufficient steam to run 6 flasks.

GOOD POINTS ABOUT THIS APPARATUS.

1. The material is digested in a 24-ounce round-bottomed flask, and therefore requires no transferring.

2. The operation is rapid. One 6-battery apparatus (which is the one illustrated) will make from 80 to 100 nitrogen distillations daily. The apparatus can be made up in duets, quartets, sextets, or any number desired.

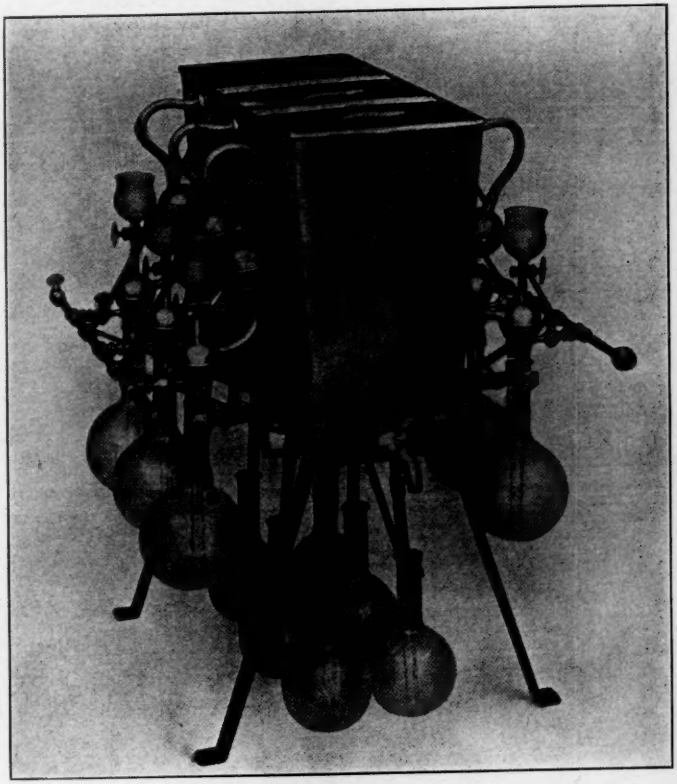
3. No glass joints and rubber tubing, therefore no leaking.

4. Large saving of gas and time.

5. Economy of space. The 6-battery apparatus, when set up ready for use, requires a space of 24 by 24 inches only.

6. The apparatus can be run with one, two, or any number of the batteries up to the limit. Each battery being independent of the other, if one determination is completed before the others, it can be recharged without any interruption to the rest of the apparatus.

7. The apparatus can be used for water analysis, in which case the solution is boiled in the flask either by gas flame or with steam, which has been purified from ammonia. This purification can be accomplished by the addition of sulphuric acid and potassium permanganate.



A NEW FORM OF ALKALIMETER.

By Charles B. Davis.

Received February 3, 1902.

THE apparatus (Fig. 1) may be described as follows: A (Fig. 2, I) is the water or acid chamber of about 10 cc. capacity, to the bottom of which is attached a bent capillary tube for the passage of the water or acid to the body of the apparatus. The liquid in this chamber is held in place by virtue of the existing pressure below and partial vacuum above the liquid, there being no stop-cocks to get out of order. B is the drying chamber which is supplied with two bent capillary tubes for the introduction of the gas into the drying material, which is generally concentrated sulphuric acid. Both chambers are supplied with

Fig. 1.

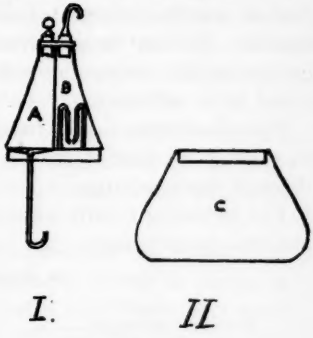


Fig. 2.

glass stoppers, and are separated by a glass partition. C (Fig. 2, II) is the body of the alkalimeter having a capacity of about 75 cc., which is intended to carry the material to be tested. The convenience of this section of the apparatus is that it may be tared on the balance, and a portion of the sample to be examined weighed directly into the alkalimeter, thus avoiding all loss caused by transferring, as in the average alkalimeter now in use. I and II are connected by an air-tight ground joint.

The alkalimeter having been thoroughly cleansed and dried, the body of the apparatus is tared, and a portion of the material to be examined, in powdered form (which should contain not more than 0.5 gram of carbonate), is weighed in together with 2 grams of a mixture of equal parts salicylic and benzoic acids.

The mixed acids I have found to give better results for all carbonates, than either alone, although either will answer the purpose in most cases.

The drying chamber is half filled with concentrated sulphuric acid, and to the water chamber is added 10 cc. distilled water freed of the gases it usually contains. Both sections are now brought together and allowed to attain the temperature of the balance.

The alkalimeter thus charged is carefully tared, and by removing both stoppers the water flows into the body of the apparatus, which causes an immediate generation of carbon dioxide; this moisture-laden gas passes through the capillary tubes into the acid of the drying chamber where it is deprived of its moisture and escapes. When this first evolution of gas ceases, the apparatus is carefully shaken, and this is repeated until no further generation of gas results. No heat is employed for the alkaline carbonates, while for the earthy carbonates a temperature as low as 55° will be found to be sufficient.

The alkalimeter is now freed of its remaining carbon dioxide by causing 0.5 liter of dry air, freed from carbon dioxide, to pass through the apparatus.

The following results were obtained with calcium, barium, and magnesium carbonates:

CARBON DIOXIDE.

	Found.	Theory.
Calcium carbonate	43.98	44.00
Barium carbonate	22.38	22.33
Magnesium carbonate	52.40	52.38

This method for estimating carbon dioxide will be found useful in the examination of baking-powders, as well as for the alkaline and earthy carbonates.

THE DETERMINATION OF LITHIA IN LEPIDOLITE.

BY W. J. SCHIEFFELIN AND W. R. LAMAR.

Received February 3, 1902.

THE J. Lawrence Smith method for decomposing the silicate is more convenient than that of dissolving in hydrofluoric acid, as the alkalies are separated from the alumina as chlorides in one step, thus avoiding two precipitates, aluminum hydroxide and barium sulphate, which are sure to hold back lithia. A

modification we have found advisable, is to remove the last traces of calcium by means of ammonium oxalate.[1] The Gooch method[2] for separating lithia from the other alkalies gives the best results. A small direct vision spectroscope is an important aid in deciding when precipitates are thoroughly washed, etc., by examining a fraction of a drop held in a looped platinum wire.

The decomposition is conducted in the usual way,[3] care being taken that the crucible is not heated too highly, as there is danger of loss of the lithium chloride, and also of the mass becoming vitrified and difficult to dissolve.

The trituration must be thorough and the leaching complete or some lithia will be held back. (The residue when treated with hydrochloric acid should leave no undecomposed mineral.)

After the dish containing the alkalies is dry, it is heated on an asbestos disk, or a triangle high above the flame, to drive off the ammonium chloride; this may take three-quarters of an hour; if it is done too rapidly, lithium chloride will go with it.

Ten cc. of hot water and one drop of hydrochloric acid will dissolve the residue in the dish, and the addition of a few drops of ammonia, and 1 or 2 drops of ammonium oxalate precipitate the remaining calcium.[4]

The chlorides of the alkalies are filtered into an Erlenmeyer flask, of thin glass (75 or 85 cc. capacity), which is placed in the air-bath, or on an asbestos disk over a small flame, and evaporated until the salts show signs of crystallizing (the solution will be down to 1 or 2 cc.); then a few drops of water are added, to effect solution, and 1 or 2 drops of concentrated hydrochloric acid to transform any hydroxide or oxychloride into chloride. Fifteen cc. of amyl alcohol (b. p. 129°–132° C.) are now added, and the flask is placed on an asbestos disk, which is slightly slanted so that the lower aqueous layer flows to one side, and the point of a Bunsen flame (1.5 inches high) is applied to the asbestos directly under the raised side of the flask. It is important to adopt this precaution as it allows the amyl alcohol to come to gentle boiling and continue boiling after all watery vapor

[1] Hillebrand: *Bull. U. S. Geol. Survey*, No. 176.

[2] *U. S. Geol. Survey Bull.* No. 42, p. 73; *Am. Chem. J.*, **9**, 33; *Proc. Am. Acad.*, p. 177 (1886); *Chem. News*, **55**, 18, 29, 40, 56, 78.

[3] Fresenius, § 140.

[4] Hillebrand: *U. S. Geol. Survey, Bull.* No. 176.

has gone off, without the tendency to bumping which causes inevitable loss.

Boiling the amyl alcohol is continued until half has evaporated. Toward the end the flame may be slightly raised and it is well to hold a thermometer in the vapor; it should read 129°–130° C., showing that the water has been driven off.

The amount of amyl alcohol remaining for the Gooch correction is judged by adding water to a flask of the same size to the same level and measuring the water.

The amyl alcohol is decanted when cold through a small filter into a weighed platinum dish; the filter is first moistened with anhydrous amyl alcohol and the residue in the flask and the filter are carefully washed with the same until free from lithia. This will require 20 cc.

The amyl alcohol is expelled from the platinum dish in a hot air-bath, under the hood, at a temperature not higher than 125° C. At this temperature it rapidly evaporates but does not boil or spatter.

After complete dryness, 0.5 cc. of concentrated sulphuric acid is added to the dish, which is warmed and rotated until all the residue has been moistened and all the chloride decomposed, and the excess of sulphuric acid is now carefully driven off by heating over a small flame or by rotating over a moderate flame. Haste in doing this will cause loss.

The lithium sulphate in the platinum dish is ignited to burn off all carbon left by the amyl alcohol, which takes but a few moments. The sulphate fuses and is kept one minute in fusion, then the dish is allowed to partially cool and covered with a watch-glass or filter-paper, to return any fragments of the fused sulphate, which sometimes splits off when it contracts.

The dish is then cooled in a desiccator and weighed; after fusing again the weight is usually found to be constant. The deduction for sodium and potassium is made as directed by Gooch.[1] That rubidium and caesium chlorides are virtually insoluble in amyl alcohol is shown by the following:

0.1022 gram rubidium chloride dissolved in water, with a drop of concentrated hydrochloric acid, treated as in the analysis with 15 cc. amyl alcohol and boiled down to 9 cc., left 0.0009 gram

[1] Deduct 0.0011 gram for each 10 cc. amyl alcohol exclusive of washings.

residual sulphates, which showed sodium strongly, also potassium, lithium and rubidium in the spectroscope.

0.1037 gram caesium chloride in the same way, with the amyl alcohol boiled down to 7 cc., left 0.001 gram residual sulphates, showing sodium, lithium, caesium, and potassium.

If the sulphate in the dish is pure, it dissolves readily in a small amount of hot water and gives a good lithium flame. To prove that the sulphate residue obtained in the analysis was lithium sulphate, the following parallel was made: An equivalent weight of pure lithium carbonate (99 per cent.) was weighed into a second platinum dish, transformed into sulphate, ignited, weighed and the lithia in both dishes determined as phosphate as directed in Fresenius, using exactly the same amounts of sodium phosphate, sodium hydroxide and ammonia wash-water, and collecting the precipitates but twice.

	Lithium sulphate.	Lithium phosphate obtained.	Lithium phosphate calculated.
	Gram.	Gram.	Gram.
A. From analysis	0.1020	0.0706	0.0717
B. From carbonate.....	0.1004	0.0670	0.0705

It will be seen that there are a number of precautions to be observed in order to avoid loss of lithia, either by leaving it behind, driving it off, or mechanically carrying it off. Good results will, however, be obtained, if care is taken to use a low red heat in the fusion; to thoroughly leach and triturate the fused mass; to avoid high heat in driving off the ammonium chloride; to avoid bumping when boiling the water out of the amyl alcohol; to filter the amyl alcohol cold; to evaporate the amyl alcohol in the dish at a temperature below its boiling-point; to drive off the sulphuric acid without any foaming or boiling; and to cover the dish while the lithium sulphate is cooling.

The analysis can be completed in two days.

LABORATORY OF SCHIEFFELIN & CO.
November 22, 1901.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, NO. 43. SENT BY H. W. WILEY.]

A NOTE ON THE USE OF THE BECHI OR SILVER NITRATE TEST ON OLIVE OILS.

BY L. M. TOLMAN.

Received January 20, 1902.

THE author, in working with a large number of salad oils, found that nearly all of them gave a brown coloration with the Bechi test, as ordinarily applied, unless the sample was first purified as described below. The modification of the reagent used was that proposed by Pearman and Moor,[1] and later by Wesson.[2]

Two grams of silver nitrate are dissolved in 200 cc. of 95 per cent. alcohol, to which 40 cc. of ether and two drops of nitric acid are added. Ten cc. of oil, 10 cc. of amyl alcohol, and 5 cc. of the reagent are mixed in a test-tube.[3] Half the mixture is poured into another test-tube and kept for comparison. The other half is heated for ten minutes in a boiling water-bath and compared with the unheated portion. The brown coloration and reduced silver show the presence of cottonseed oil. Treated in this way, some oils which were especially rancid gave a strong test with the Bechi reagent, but from the physical and chemical constants and the Halphen reaction cottonseed oil could not have been present.

It has been advised to heat the oil for one hour at 100°, but this, while it reduced the reaction of the reagent with other oils, also weakened the reaction with cottonseed oil and was not at all satisfactory.

Wesson advises treatment with 2 per cent. nitric acid, but while this purified the oil in some cases it could not be depended on always, since quite a number of the oils treated in this way gave strong reactions although they contained no cottonseed oil.

The use of a dilute alkali works very well but is inconvenient, for it emulsifies and separates very slowly. A method which is much easier, more rapid, and one which gives very satisfactory results is as follows:

To about 25 cc. of the oil add 25 cc. of 95 per cent. alcohol,

[1] Allen's "Commercial Organic Analysis," Vol. II, Part I, second edition, p. 143.

[2] This Journal, 17, 724.

[3] Amyl alcohol is used to dissolve the fats or oils and thus secure a much better mixture with the reagent.

heat gently, and shake vigorously; allow to stand until the liquids separate, decant as much of the alcohol solution as possible, and then wash the residue with 2 per cent. nitric acid and finally with water. Cottonseed oils treated in this manner reacted with undiminished strength, while the olive oils which before treatment gave deep brown colorations, showed after treatment no coloration or reduction of the silver solution at all. The free fatty acids and other products of rancidity, which are evidently the cause of the brown coloration with the Bechi reagent which these oils give, are dissolved by the alcohol and removed while the reducing principle of the cottonseed oil is not affected. This method can be readily applied to lards or other fats which it is desirable to test by the Bechi reagent. The writer was able, by this method, to get very satisfactory and reliable results.

A STUDY OF THE BECHI TEST FOR COTTONSEED OIL.

By Augustus H. Gill and Charles H. Dennison.

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WHILE in the case of sesame oil the substances to which the Baudouin test is due may be said to be fairly well known,[1] such is not the case with the test in question. Some[2] consider that it is due to a sulphur compound in the oil and others[3] to an aldehydic body. While the evidence given by this paper is not conclusive, it was thought sufficiently interesting to publish.

The tests made by these various experimenters were repeated and confirmed; it was found that an oil heated to 260° gave neither the Bechi-Milliau test nor the Halphen test. This might indicate that the active principle of both tests was the same but for the fact that Raikow,[4] by oxidizing the oil with potassium permanganate and sulphuric acid, obtained an oil which gave the Bechi test but not the Halphen.

TESTS FOR ALDEHYDIC BODIES.

400 cc. of oil were shaken with an equal quantity of strong sodium bisulphite solution for twelve hours; the oil upon separation gave the Bechi test although a longer time was required for

[1] Villavecchia and Fabris: Abstr. *J. Soc. Chem. Ind.*, **16**, 1045.
[2] Dupont: *Bull. Soc. Chim.*, **13**, 696; Charabot and March: *Ibid.*, **21**, 552.
[3] Holde: *J. Soc. Chem. Ind.*, **11**, 637; Wilson: *Chem News*, **59**, 99.
[4] *Chem. Zig.*, **24**, 562, 583.

its development and it appeared in less intensity. This was repeated with similar results; in this latter case crystals separated, which on being distilled with sodium carbonate gave no aldehyde reaction with the fuchsine-aldehyde reagent.

A portion of the oil was treated with dry ammonia gas for seven hours; there was no indication of any crystalline compound of aldehyde ammonia having been formed, and the oil gave the Bechi-Milliau test with even greater intensity.

TEST FOR SULPHUR COMPOUNDS.

In two cases only the black compound formed by the action of silver nitrate upon the fatty acid gave off hydrogen sulphide; this was recognized by its odor and blackening lead acetate paper. If, however, sulphur compounds were present in the fatty acid sufficient to blacken silver nitrate, it would seem as if other metallic salts should show characteristic colors. Salts of cadmium, lead, copper, and mercury were tried with negative results except that with the mercury salts reduction to metallic mercury took place.

In the repetition of Dupont's work both the aqueous distillate from the unheated oil and the oil itself gave the Bechi test. This was not the case with the oil which had been heated to 260°. In conclusion, in view of the fact that bodies of an aldehydic character could not be detected in the oil by either the fuchsine aldehyde reagent, by sodium bisulphite, or by ammonia, it would seem that it was not likely that they were present. This would seem to be confirmed by Raikow's oxidation with permanganate and sulphuric acid. The evidence would seem to favor the presence of sulphur compounds.

NEW BOOKS.

STUDIES FROM THE CHEMICAL LABORATORY OF SHEFFIELD SCIENTIFIC SCHOOL. EDITED BY HORACE L. WELLS. Vol. I, xi + 444 pp. Vol. II, ix + 379 pp. New York: Charles Scribner's Sons. 1901. Price, $7.50 per set.

In consequence of the recent bicentennial celebration of Yale University, there has been presented to the world "a series of volumes * * * prepared * * * and issued * * * as a partial indication of the character of the studies in which the University teachers are engaged." Two volumes of this series,

bearing the title given in the head lines, have been placed in the hands of the writer, who has read them with the greatest pleasure. The first volume contains a brief sketch of the Sheffield Laboratory, including a list of the publications (131) of the present officials of the department and their colaborers, followed by a series of papers in detail relating to general inorganic chemistry. Although the writer had studied these investigations as they appeared in print in the various journals, he can truthfully say that from the moment his attention was again attracted to the first lines of the first article which read "in the course of some experiments with caesium compounds, bromine was added to a concentrated solution of caesium chloride with an astonishing result," his interest in the remarkable results obtained in the preparation and study of double halides, by Professor Wells and his associates, was revived; indeed, this interest became so great that he read on and on, through one paper after the other, unconscious of his surroundings and the flight of time until the final paragraph was reached, when the book was closed with the conviction that it was overflowing with facts, bristling with suggestions, and deserving of the most careful study by all chemists, but especially those who fail to realize the immense work remaining to be done in the inorganic field. Five hundred double halides have been studied, more than a third of which have been made in the Yale laboratory. It is not very surprising then to read in the final chapter, "that the valency of a negative halide has no influence upon the types of double salts that it forms;" that "molecules of alkaline halides possess nearly the same combining power as negative halides; that double halides probably increase in ease of formation and variety from the iodides to the fluorides," and then "some indications of regularity have been observed in connection with these researches, but it must be admitted that the results have been negative as far as throwing light upon the structure of this class of compounds is concerned."

While the prevailing thought in Volume I is "double halogen salts," we meet in the companion volume anilides, formyl derivatives, amidines, imido esters, thiazoles, urea amidines, acyclic benzoyl pseudoureas and thiosemicarbazidic esters—all attesting, by the skilful way in which they have been prepared and studied, the keen originating power, and the untiring energy and zeal of their various authors. Just a bit of the "double halide" spirit

has found its way into several of these organic papers, for upon p. 34 will be noticed

$$(C_6H_4NO_2.NH.CO.CH_3)_2HBr.Br_2,$$
$$(C_6H_4NO_2.NH.CO.CH_3)_2HBr.Br_4, \text{ etc.},$$

which are perfectly analogous to the perhalides $CsBr.Br_2$, $CsI.I_4$, and $NH_4Br.Br_2$. This slight digression into the field that received such ample consideration in the first volume is most pardonable, nay, it is desirable and should be pursued farther whenever it is at all possible. Much more might be said, but as the character of the volumes is now in a measure indicated, the writer would conclude with the recommendation that the reader of these lines should study the papers for himself, feeling assured that when he has done so, he will concur with the writer in the opinion that these researches not only reflect great credit upon their authors and the university in which they were planned, but that they will be real incentives to the great body of young, enthusiastic chemists to go forward and do likewise.

EDGAR F. SMITH.